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PATENT ABSTRACTS OF JAPAN

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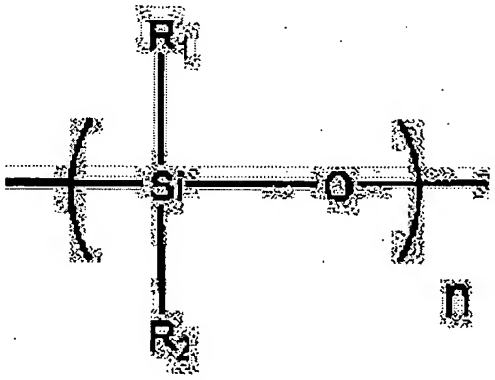
(72)Inventor : ONO MICHIO
SEN SHOICHI

(54) POLYSILOXANE SALT, ELECTROLYTE COMPOSITION, ELECTROCHEMICAL BATTERY, NONAQUEOUS SECONDARY BATTERY AND PHOTOELECTROCHEMICAL BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide new polysiloxane salt substantially non-volatile with excellent electrification transportation ability, and a new electrolyte composition containing salt, and to provide an electrochemical battery comprising the electrolyte composition and having excellent durability and ion conductivity, a photoelectrochemical battery with excellent durability and optical transfer characteristic, and a nonaqueous secondary battery not lowered in battery capacity and having excellent cycle property.



一般式 (I)

SOLUTION: This electrolyte composition is characterized by containing the salt that has in structure an atomic group expressed by general formula (I); an anion part formed by dissociating proton from one selected out of sulfonamide, a disulfon imide, N-acyl sulfonamide, alcohol, phenol and sulfonic acid; and a cation part which is metal ion and/or organic cation belonging to the group I or group II of the periodic table. The electrochemical battery contains electrolyte composition.

LEGAL STATUS

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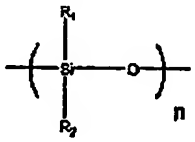
最終頁に続く

(54)【発明の名称】　ポリシロキサン塩，電解質組成物，電気化学電池，非水二次電池及び光電気化学電池

(57)【要約】
【課題】　実質的に揮発せず，かつ電化輸送能に優れた新規なポリシロキサン塩及び該塩を含有する新規な電解質組成物を提供し，さらに該電解質組成物を含み，耐久性とイオン伝導性に優れた電気化学電池，耐久性と光変換特性に優れた光電気化学電池，及び電池容量を低下させず，しかもサイクル特性に優れた非水二次電池を提供する。
【解決手段】　下記一般式（I）で表される原子団と，スルホンアミド，ジスルホンイミド，N－アシルスルホンアミド，アルコール，フェノール又はスルホン酸から選択されるいずれかからプロトンが解離してなるアニオン部と，周期律表第1族又は第2族に属する金属イオン及び／又は有機カチオンのいずれかであるカチオン部と，を構造中に有する塩を含有することを特徴とする電解質組成物，及び該電解質組成物を含有する電気化学電池である。
【化1】



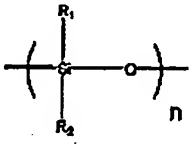
一般式（I）

1

【特許請求の範囲】

【請求項１】 下記一般式（Ｉ）で表される原子団と、スルホンアミド．ジスルホンイミド．Ｎ－アシルスルホンアミド、アルコール、フェノール及びスルホン酸のうち少なくとも１つからプロトンが解離してなるアニオン部と．周期律表第１族又は第２族に属する金属イオン及び／又は有機カチオンであるカチオン部と、を構造中に有する塩を含有することを特徴とする電解質組成物。

【化１】



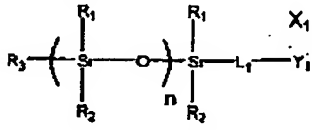
一般式（Ｉ）

2

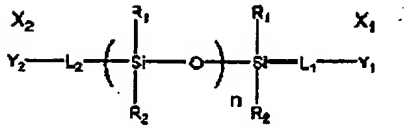
＊前記一般式（Ｉ）において．R_1．R_2は、アルキル基、アリール基又はアルコキシ基を表す。ｎは３以上の数を表す。

【請求項２】 前記塩が．下記一般式（ＩＩＩ－ａ）及び下記一般式（ＩＩＩ－ｂ）のいずれかの構造で表される塩である請求項１に記載の電解質組成物。

【化２】



一般式(III-a)



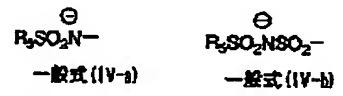
一般式(III-b)

前記一般式（ＩＩＩ－ａ）及び前記一般式（ＩＩＩ－ｂ）において．R_1及びR_2は、各々独立にアルキル基を表す。X_1及びX_2は、各々独立に、前記カチオン部を表す。X_1及びX_2は互いに同じであっても異なってもよい。L_1及びL_2は、アルキレン基を含んだ２価連結基を表す。Y_1及びY_2は、前記アニオン部を含む置換基を表す。Y_1及びY_2は互いに同じであっても異なってもよい。R_3は．置換若しくは無置換のアルキル基を表す。ｎは３以上の数を表す。

【請求項３】 前記R_1及びR_2が炭素原子数１～３のアルキル基であり．前記L_1及びL_2が各々独立に－（ＣＨ$_2$）$_2$－及び－（ＣＨ$_2$）$_2$ＯＣＨ$_2$ＣＨ$_2$－のいずれかで表される２価連結基であり．Y_1及びY_2が各々独立に下記一般式（ＩＶ－ａ）及び一般式（ＩＶ－ｂ）のいずれかの構造で表されるアニオン部を含む置換基である請求項※

※１又は２に記載の電解質組成物。

【化３】



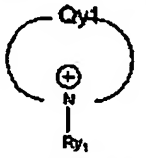
一般式(IV-a)　　一般式(IV-b)

前記一般式（ＩＶ－ａ）及び一般式（ＩＶ－ｂ）において．R_3は炭素原子数１～３のアルキル基を表す。

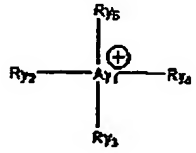
【請求項４】 前記カチオン部が、リチウムイオンである請求項１から３のいずれかに記載の電解質組成物。

【請求項５】 前記カチオン部が、一般式（ＩＩ－ａ）．一般式（ＩＩ－ｂ）．及び一般式（ＩＩ－ｃ）で表されるカチオン部のうちいずれかである請求項１から３のいずれかに記載の電解質組成物。

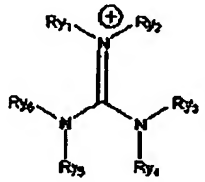
【化４】



一般式(II-a)



一般式(II-b)



一般式(II-c)

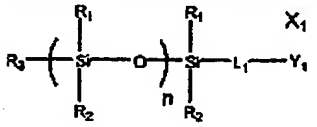
前記一般式（ＩＩ－ａ）において、Q_{y1}は、窒素原子とともに、５員環又は６員環の芳香族カチオンを形成しうる原子団を表す。R_{y1}は．置換若しくは無置換のアルキル基又はアルケニル基を表す。前記一般式（ＩＩ－ｂ）において、A_{y1}は、窒素原子又はリン原子を表す。

R_{y1}．R_{y2}、R_{y3}及びR_{y4}は、置換若しくは無置換のアルキル基、又は置換若しくは無置換のアルケニル基を表す。また、R_{y1}．R_{y2}、R_{y3}及びR_{y4}のうち、２以上が互いに連結してA_{y1}を含む非芳香族環を形成してもよい。前記一般式（ＩＩ－ｃ）において．R_{y1}、R_{y2}、R

₁．R₁₀、R₁₁及びR₁₂は．置換若しくは無置換のアルキル基又は置換若しくは無置換のアルケニル基を表し、それらのうち．２つ以上が互いに連結して環構造を形成してもよい。前記一般式（ＩＩ－ａ）．一般式（ＩＩ－ｂ）．及び一般式（ＩＩ－ｃ）で表される化合物は、Q₁₁又はR₁₁～R₁₂を介して多量体を形成してもよい。

【請求項６】　請求項１から５のいずれかに記載の電解質組成物を含むことを特徴とする電気化学電池。

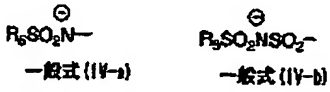
【請求項７】　請求項１から５のいずれかに記載の電解＊



一般式(III-a)

前記一般式（ＩＩＩ－ａ）及び前記一般式（ＩＩＩ－ｂ）において．R₁及びR₂は、各々独立に炭素原子数１～３のアルキル基を表す。X₁及びX₂は、リチウムイオンを表す。L₁及びL₂は．各々独立に－（ＣＨ₂）₂－及び－（ＣＨ₂）₂ＯＣＨ₂ＣＨ₂－のいずれかで表される２価連結基を表す。Y₁及びY₂は、各々独立に下記一般式（ＩＶ－ａ）及び一般式（ＩＶ－ｂ）のいずれかの構造で表されるアニオン部を含む置換基を表す。R₃は、置換若しくは無置換のアルキル基を表す。ｎは３以上の数を表す。

【化６】



一般式(IV-a)　　一般式(IV-b)

前記一般式（ＩＶ－ａ）及び一般式（ＩＶ－ｂ）において．R₄は炭素原子数１～３のアルキル基を表す。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は．ポリシロキサン塩．電解質組成物、電気化学電池、非水二次電池及び光電気化学電池に関し、さらに詳しくは．電池、及び他の電気化学デバイス材料として好適な新規なポリシロキサン塩（以下「電解質塩」と称する場合もある）及び当該塩を含有する電解質組成物．並びに当該電解質組成物を用いた電気化学電池、特に非水電解液二次電池及び光電気化学電池に関する。

【０００２】

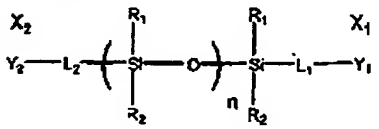
【従来の技術】非水二次電池や色素増感太陽電池などの電気化学電池に用いられる電解質とは．目的に応じたイオンを含み、そのイオンを電極間に輸送する機能（イオン伝導という）を持つ媒体である。例えば、非水二次電池の代表であるリチウム二次電池では．リチウムイオンの輸送が、色素増感太陽電池では、ヨウ素イオン及びヨウ素三量体イオンの伝導性が問題となる。これら電池に

＊質組成物を含むことを特徴とする非水二次電池。

【請求項８】　請求項１から５のいずれかに記載の電解質組成物を含む電荷移動層と、色素で増感された半導体を含む感光層と．対向電極と、を有することを特徴とする光電気化学電池。

【請求項９】　下記一般式（ＩＩＩ－ａ）及び下記一般式（ＩＩＩ－ｂ）のいずれかの構造で表されることを特徴とするポリシロキサン塩。

【化５】



一般式(III-b)

おいては、一般に、イオン伝導性が高い溶液系が電解質として多く用いられているが、電池に組み込んだ際の溶媒の詰まや漏れが電池の耐久性を低下させるなどの問題がある。即ち．一般的な低分子溶媒を使用した電解質を電池に組み込んだ場合は．溶媒の揮発や液漏れによる電池性能が劣化するという問題がある。また、リチウム二次電池においては溶液を密閉するため．金属容器を用いなければならず．電池質量が重くなり．電池形状にも自由度を持たせることが困難という問題がある。

【０００３】前記溶液系電解質の欠点を克服するため、近年．様々の電解質が提案されている。溶液電解質をポリマーマトリックスに浸潤させたいわゆるゲル電解質は．溶液系電解質に対して．イオン伝導度の低下が小さく電池性能を落とさないが．溶媒の揮発を完全に抑止することはできていないという問題がある。また．塩をポリエチレンオキシドなどのポリマーに溶解したポリマー電解質は、溶液系電解質の問題を解決するものとして期待されるが．イオン伝導度は未だ十分ではないという問題がある。

【０００４】一方、室温で液体の塩をベースとした、いわゆる溶融塩電解質を用いる方法が知られているが、低沸点の化合物を含まないため揮発による電池性能の劣化を防止するには有効である反面、一般に粘度が高いため電荷輸送能が低いという問題がある。例えば、対アニオンがＢＦ₄⁻、（ＣＦ₃ＳＯ₂）₂Ｎ⁻などのイミダゾリウム塩やピリジニウム塩は、室温で液状の室温溶融塩であり．リチウムイオン電池用の電解質として、提案されているが、電解質の機械的強度とイオン伝導性とは相反し．溶融塩自身の粘性を上げたり、ポリマーを含有させるなどの手段で．機械的強度を強くした場合にはイオン伝導度の低下が見られる。さらに、上記のような電解質では．イオン伝導性の温度依存性が大きく、特に低温でのイオン伝導性が不十分という問題がある。

【０００５】ところで、光エネルギーを電気エネルギーに変換する太陽光発電は単結晶シリコン太陽電池．多結

晶シリコン太陽電池、アモルファスシリコン太陽電池、テルル化カドミウムやセレン化インジウム銅等の化合物太陽電池が実用化、若しくは研究開発の対象となっているが、普及させる上で製造コスト、原材料の確保、エネルギーペイバックタイムの長さなどの問題点を克服する必要がある。一方、大面積化や低価格化を指向した有機材料を用いた太陽電池もこれまでに多く提案されているが、変換効率が低く、耐久性も悪いという問題がある。

【０００６】こうした状況の中で、Ｎａｔｕｒｅ（第３５３巻、第７３７～７４０頁、１９９１年）及び米国特許４９２７７２１号等に、色素によって増感された酸化物半導体を用いた光電変換素子（以後、色素増感光電変換素子と略す）及びこれを用いた光電気化学電池の技術が開示された。この電池は負極として機能する光電変換素子、電荷移動層及び対極からなる。光電変換素子は導電性支持体及び感光層からなり、感光層は表面に色素が吸着した半導体を含む。電荷移動層は酸化還元体からなり、負極と対極（正極）との間で電荷輸送を担う。上記特許で提案された光電気化学電池では、電荷移動層としてヨウ化カリウム等の塩を電解質とする水溶液（電解液）が用いられた。この方式は安価で、比較的高いエネルギー変換効率（光電変換効率）が得られる点で有望であるが、長期にわたって使用すると電解液の蒸散、枯渇により光電変換効率が著しく低下したり、電池として機能しなくなることが問題である。

【０００７】こうした問題に対し、電解液の枯渇防止方法として、ＷＯ９５／１８４５６号に低融点化合物であるイミダゾリウム塩を電解質とする方法が記載されている。この方法によれば、従来、電解質の溶媒として用いていた水や有機溶剤が不要、あるいは少量で済むため、耐久性の改善は見られたが、未だ耐久性は不十分である。またイミダゾリウム塩を高濃度にすると粘度が高くなるとともに電荷輸送能が低下し、光電変換効率が低くなるという問題があった。さらには、トリアゾリウム塩を電解質とする方法もあるが、この方法においてもイミダゾリウム塩と同様の問題がある。

【０００８】非水二次電池などの電気化学電池に用いられる電解質においても溶液系電解質の欠点を克服するため、近年、電解質の固体化（ポリマー電解質）が研究されている。塩をポリエチレンオキシドなどのポリマーに溶解したポリマー電解質は、溶液系電解質の問題を解決するものとして期待されるが、イオン伝導度は未だ十分ではない。また、これまで主に報告されてきたポリマー電解質では、電解質の重要な特性のひとつである、イオン輸率（例えば、リチウム二次電池の場合は、リチウムイオン輸率）が一般的に低い。そのため、例えばリチウム二次電池の場合充放電電流が時間と共に減少し、容量の低下を招くなどの問題を引き起こし、汎用性のある商品に組み込むことは困難であるのが実情である。

【０００９】

【発明が解決しようとする課題】本発明は、前記従来における問題を解決し、以下の目的を達成することを課題とする。即ち、本発明は、実質的に揮発せず、かつ電化輸送能に優れた新規なポリシロキサン塩及び該塩を含有する新規な電解質組成物を提供し、さらに該電解質組成物を含み、耐久性とイオン伝導性に優れた電気化学電池、耐久性と光変換特性に優れた光電気化学電池、及び電池容量を低下させず、しかもサイクル特性に優れた非水二次電池を提供することを目的とする。

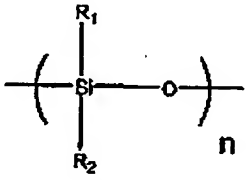
【００１０】

【課題を解決するための手段】前記課題を解決するための手段は、以下の通りである。

＜１＞　下記一般式（Ｉ）で表される原子団と、スルホンアミド、ジスルホンイミド、Ｎ－アシルスルホンアミド、アルコール、フェノール及びスルホン酸のうち少なくとも１つからプロトンが解離してなるアニオン部と、周期律表第１族又は第２族に属する金属イオン及び／又は有機カチオンであるカチオン部と、を構造中に有する塩を含有することを特徴とする電解質組成物である。

【００１１】

【化７】



一般式（Ｉ）

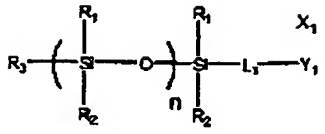
【００１２】前記一般式（Ｉ）において、R_1、R_2は、アルキル基、アリール基又はアルコキシ基を表す。ｎは３以上の数を表す。

【００１３】＜２＞　前記塩が、下記一般式（ＩＩＩ－ａ）及び下記一般式（ＩＩＩ－ｂ）のいずれかの構造で表される塩である前記＜１＞に記載の電解質組成物である。

【００１４】

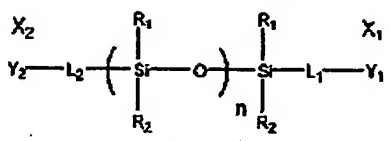
【化８】

7



一般式(III-a)

8



一般式(III-b)

【００１５】前記一般式（ＩＩＩ－ａ）及び前記一般式（ＩＩＩ－ｂ）において．R_1及びR_2は、各々独立にアルキル基を表す。X_1及びX_2は、各々独立に、前記カチオン部を表す。X_1及びX_2は互いに同じであっても異なってもよい。L_1及びL_2は．アルキレン基を含んだ２価連結基を表す．Y_1及びY_2は、前記アニオン部を含む置換基を表す。Y_1及びY_2は互いに同じであっても異なってもよい。R_3は、置換若しくは無置換のアルキル基を表す。ｎは３以上の数を表す。

【００１６】＜３＞　前記R_1及びR_2が炭素原子数１～３のアルキル基であり、前記L_1及びL_2が各々独立に－$(CH_2)_3$－及び－$(CH_2)_2OCH_2CH_2$－のいずれかで表される２価連結基であり、Y_1及びY_2が各々独立に下記一般式（ＩＶ－ａ）及び一般式（ＩＶ－ｂ）のいずれかの構造で表されるアニオン部を含む置換基である前記＜１＞又は＜２＞に記載の電解質組成物である。

【００１７】

＊【化９】

一般式(IV-a)　　一般式(IV-b)

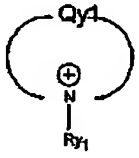
【００１８】前記一般式（ＩＶ－ａ）及び一般式（ＩＶ－ｂ）において．R_3は炭素原子数１～３のアルキル基を表す。

【００１９】＜４＞　前記カチオン部が、リチウムイオンである前記＜１＞から＜３＞のいずれかに記載の電解質組成物である。

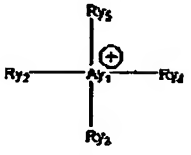
【００２０】＜５＞　前記カチオン部が、一般式（ＩＩ－ａ）、一般式（ＩＩ－ｂ）、及び一般式（ＩＩ－ｃ）で表されるカチオン部のうちいずれかである前記＜１＞から＜３＞のいずれかに記載の電解質組成物である。

【００２１】

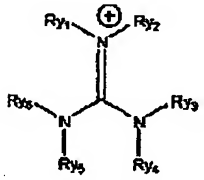
＊【化１０】



一般式(II-a)



一般式(II-b)



一般式(II-c)

【００２２】前記一般式（ＩＩ－ａ）において．Q$_{y1}$は．窒素原子とともに．５員環又は６員環の芳香族カチオンを形成しうる原子団を表す。R_{y1}は、置換若しくは無置換のアルキル基又はアルケニル基を表す。前記一般式（ＩＩ－ｂ）において．A_{y1}は．窒素原子又はリン原子を表す。R_{y2}、R_{y3}．R_{y4}及びR_{y5}は、置換若しくは無置換のアルキル基、又は置換若しくは無置換のアルケニル基を表す。また、R_{y2}、R_{y3}．R_{y4}及びR_{y5}のうち．２以上が互いに連結してA_{y1}を含む非芳香族環を形成してもよい。前記一般式（ＩＩ－ｃ）において．R_{y1}．R_{y2}、R_{y3}、R_{y4}．R_{y5}及びR_{y6}は、置換若しくは無置換のアルキル基又は置換若しくは無置換のアルケニル基を表し．それらのうち、２つ以上が互いに連結して環構造を形成してもよい。前記一般式（ＩＩ－ａ）、一般式（ＩＩ－ｂ）、及び一般式（ＩＩ－ｃ）で表される化合物は、Q$_{y1}$又はR_{y1}～R_{y6}を介して多量体を形成してもよい。

【００２３】＜６＞　前記＜１＞から＜５＞のいずれかに記載の電解質組成物を含むことを特徴とする電気化学電池である。

【００２４】＜７＞　前記＜１＞から＜５＞のいずれかに記載の電解質組成物を含むことを特徴とする非水二次電池である。

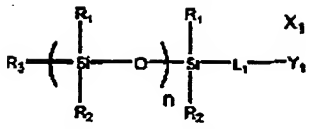
【００２５】＜８＞　前記＜１＞から＜５＞のいずれかに記載の電解質組成物を含む電荷移動層と、色素で増感された半導体を含む感光層と、対向電極と、を有することを特徴とする光電気化学電池である。

【００２６】＜９＞　下記一般式（ＩＩＩ－ａ）及び下記一般式（ＩＩＩ－ｂ）のいずれかの構造で表されることを特徴とするポリシロキサン塩である。

【００２７】

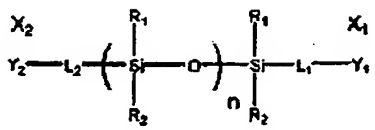
【化１１】

9



一般式(III-a)

10



一般式(III-b)

【００２８】前記一般式（ＩＩＩ－ａ）及び前記一般式（ＩＩＩ－ｂ）において．R_1及びR_2は、各々独立に炭素原子数１～３のアルキル基を表す。X_1及びX_2は、リチウムイオンを表す。L_1及びL_2は．各々独立に－（CH_2）$_2$－及び－（CH_2）$_2$$OCH_2CH_2$－のいずれかで表される２価連結基を表す。$Y_1$及び$Y_2$は、各々独立に下記一般式（ＩＶ－ａ）及び一般式（ＩＶ－ｂ）のいずれかの構造で表されるアニオン部を含む置換基を表す。R_3は、置換若しくは無置換のアルキル基を表す。ｎは３以上の数を表す。

【００２９】

【化１２】

一般式(IV-a)　一般式(IV-b)

【００３０】前記一般式（ＩＶ－ａ）及び一般式（ＩＶ－ｂ）において．R_3は炭素原子数１～３のアルキル基を表す。

【００３１】

【発明の実施の形態】以下．本発明のポリシロキサン塩．電解質組成物、電気化学電池、非水二次電池及び光電気化学電池について説明する。ここではまず．本発明のポリシロキサン塩及び該塩を含有する電解質組成物について詳細に説明する。

【００３２】（塩及び電解質組成物）本発明の電解質組成物は、化学反応及び金属メッキ等の反応溶媒．ＣＣＤ（電荷結合素子）カメラ．種々の電気化学電池（いわゆる電池）等に用いられる。好ましくは非水二次電池（特に．リチウム二次電池）又は下記の半導体を用いた光電気化学電池に用いられ、光電気化学電池に用いることがより好ましい。

【００３３】本発明の塩は．前記一般式（Ｉ）で表される原子団と、スルホンアミド、ジスルホンイミド．Ｎ－アシルスルホンアミド、アルコール．フェノール又はスルホン酸のうち少なくとも１つからプロトンが解離してなるアニオン部と、周期律表第１族又は第２族に属する金属イオン及び／又は有機カチオンであるカチオン部と．を構造中に有することを特徴とする。本発明の電解質組成物は、前記塩を含有する電解質組成物であることを特徴とする。

【００３４】＜一般式（Ｉ）で表される原子団＞本発明の塩に含まれる前記一般式（Ｉ）で表される原子団について詳述する。

【００３５】前記一般式（Ｉ）において、R_1、R_2は、各々独立にアルキル基〔好ましくは炭素原子数（以下Ｃ数と称する場合がある）が１～２４であり、より好ましくはＣ数１～１０であり．直鎖状であっても分岐鎖状であってもよく．例えばメチル、エチル．プロピル．ブチル．．ｉ－プロピル、ｉ－ブチル、ペンチル、ヘキシル、オクチル、２－エチルヘキシル、ｔ－オクチル．デシル．ドデシル．テトラデシル、２－ヘキシルデシル、ヘキサデシル、オクタデシル．シクロヘキシルメチル、オクチルシクロヘキシル〕．アリール基〔好ましくはＣ数６～２４であり．より好ましくはＣ数６～１０であり、例えばフェニル．ナフチル〕、又はアルコキシ基〔好ましくはＣ数１～２４、例えばメトキシ．エトキシ．ブトキシ．オクチルオキシ、メトキシエトキシ、メトキシペンタ（エチルオキシ）、アクリロイルオキシエトキシ、ペンタフルオロプロポキシ〕を表す。さらにこれらR_1、R_2は、置換基を有していてもよく、好ましい置換基としては、置換していてもよいアルキル基〔好ましくはＣ数１～２４であり、より好ましくはＣ数１～１０であり．直鎖状であっても分岐鎖状であってもよく．例えばメチル、エチル、プロピル、ブチル．ｉ－プロピル、ｉ－ブチル、ペンチル、ヘキシル、オクチル、２－エチルヘキシル、ｔ－オクチル．デシル．ドデシル．テトラデシル、２－ヘキシルデシル、ヘキサデシル、オクタデシル．シクロヘキシルメチル、オクチルシクロヘキシル〕．置換していても縮環していてもよいアリール基（好ましくはＣ数６～２４．例えばフェニル、４－メチルフェニル、３－シアノフェニル、２－クロロフェニル．２－ナフチル）、置換していても縮環していてもよい複素環基（含窒素複素環基のときは環中の窒素が４級化していてもよい。好ましくはＣ数２～２４、例えば４－ピリジル、２－ピリジル．１－オクチルピリジニウム－４－イル、２－ピリミジル、２－イミダゾリル．２－チアゾリル）．アルコキシ基〔好ましくはＣ数１～２４．例えばメトキシ、エトキシ、ブトキシ、オクチルオキシ．メトキシエトキシ．メトキシペンタ（エチルオキシ）．アクリロイルオキシエトキシ．ペンタフルオロプロポキシ〕、アシルオキシ基（好ましくはＣ数１～２４．例えばアセチルオキシ．ベンゾイルオキシ）．アルコキシカルボニル基（好ましくはＣ数２～２４．例えばメトキシカルボニル、エトキシカルボニル）、シアノ基．フルオロ基．アルコキシカルボニル基、シアノ基、及び重合性基（好ましくはビニル基．アクリロイル基、メタクリロイル基、スチリル基、桂皮酸残基など）が挙げられる。前記一般式（Ｉ）において．ｎは３以上の数

を表す。

【0036】<アニオン部>本発明の塩を構成するアニオン部は、スルホンアミド．ジスルホンイミド．N－アシルスルホンアミド、アルコール、フェノール．スルホン酸のうちすくなくとも1つからプロトンが解離してなるアニオンである。前記アニオン部としては、スルホンアミド、ジスルホンイミド．N－アシルスルホンアミドが好ましい。

【0037】アニオン部の共役酸は．pKaが11以下であることが好ましく、7以下であることがより好ましい。

【0038】<カチオン部>本発明の塩を構成するカチオン部が周期律表第1（Ia）又は第2（IIa）族に属する金属イオンである場合、一般式（I）で示される原子団は、オキシアルキレン基と異なりカチオンと強く相互作用せず．運動性が高いことから．柔軟なイオン伝導場を提供する。それにより高いイオン輸率とイオン伝導性が実現される。

【0039】本発明の塩を構成するカチオン部としては．前記一般式（III－a）、前記一般式（III－b）及び前記一般式（III－c）のいずれかで表される有機カチオン、及び／又はリチウムイオンが好ましい。

【0040】前記一般式（III－a）において．Q_{11}は．窒素原子とともに．5員環又は6員環の芳香族カチオンを形成しうる原子団を表す。R_{11}は、置換若しくは無置換のアルキル基又はアルケニル基を表す。

【0041】前記一般式（III－b）において．A_{11}は．窒素原子又はリン原子を表す。R_{11}、R_{12}．R_{13}及びR_{14}は、置換若しくは無置換のアルキル基又はアルケニル基を表す。また、R_{11}、R_{12}．R_{13}及びR_{14}のうち2つ以上が互いに連結してA_{11}を含む非芳香族環を形成してもよい。

【0042】前記一般式（III－c）において．R_{11}、R_{12}．R_{13}、R_{14}、R_{15}及びR_{16}は．置換若しくは無置換のアルキル基又はアルケニル基を表し、それらのうち2以上が互いに連結して環構造を形成してもよい。

【0043】前記一般式（III－a）．前記一般式（III－b）、及び前記一般式（III－c）で表されるカチオンは、Q_{11}又はR_{11}～R_{16}を介して多量体を形成してもよい。

【0044】前記一般式（III－a）において、窒素とともに芳香族5又は6員環のカチオンを形成しうる原子団Q_{11}の構成原子は、好ましくは炭素．水素、窒素、酸素．硫黄より選択される。

【0045】Q_{11}で完成される6員環としては．好ましくは．ピリジン．ピリミジン、ピリダジン、ピラジン、トリアジンであり、より好ましくはピリジンである。

【0046】Q_{11}で完成される芳香族5員環としては、好ましくはオキサゾール．チアゾール．イミダゾール、ピラゾール、イソオキサゾール、チアジアゾール．オキサジアゾール．トリアゾールであり．より好ましくはオキサゾール、チアゾール．イミダゾールである。特に好ましくは、オキサゾール．イミダゾールである。

【0047】前記一般式（III－a）．前記一般式（III－b）及び前記一般式（III－c）において．R_{11}～R_{16}は、置換若しくは無置換のアルキル基（好ましくは炭素原子数（以下C数）が1～24であり、直鎖状であっても分岐鎖状であってもよく、また環式であってもよい。例えばメチル、エチル．プロピル．ブチル．i－プロピル、ペンチル、ヘキシル、オクチル、2－エチルヘキシル、t－オクチル、デシル、ドデシル、テトラデシル．2－ヘキシルデシル．オクタデシル、シクロヘキシル．シクロペンチル）、重合性基（好ましくはビニル基．アクリロイル基、メタクリロイル基、スチリル基、桂皮酸残基など）、置換若しくは無置換のアルケニル基（好ましくはC数が2～24であり．直鎖状であっても分岐鎖状であってもよい。例えば、ビニル、アリル）を表し．好ましくはC数3～18のアルキル基又はC数2～18のアルケニル基を表し、より好ましくはC数4～6のアルキル基を表す。

【0048】前記一般式（III－a）．前記一般式（III－b）及び前記一般式（III－c）において．Q_{11}及びR_{11}～R_{16}は．置換基を有していてもよい。好ましい置換基の例としては、ハロゲン原子（F，Cl、Br，I）．シアノ基．アルコキシ基（メトキシ、エトキシ、メトキシエトキシなど）．アリーロキシ基（フェノキシなど）、アルキルチオ基（メチルチオ．エチルチオなど）．アシル基（アセチル．プロピオニル、ベンゾイルなど）、スルホニル基（メタンスルホニル、ベンゼンスルホニルなど）．アシルオキシ基（アセトキシ．ベンゾイルオキシなど）、スルホニルオキシ基（メタンスルホニリオキシ、トルエンスルホニルオキシなど）．ホスホニル基（ジエチルホスホニルなど）．アミド基（アセチルアミノ、ベンゾイルアミドなど）．カルバモイル基（N，N－ジメチルカルバモイル、N－フェニルカルバモイルなど）．アルキル基（メチル．エチル、プロピル．イソプロピル、シクロプロピル．ブチル、2－カルボキシエチル．ベンジルなど）、アリール基（フェニル．トルイルなど）、複素環基（例えば、ピリジル、イミダゾリル、フラニルなど）、アルケニル基（ビニル、1－プロペニルなど）などが挙げられる。

【0049】<塩構造>本発明の塩として好ましいのは．前記一般式（III－a）又は前記一般式（III－b）で表されるポリシロキサン塩である。

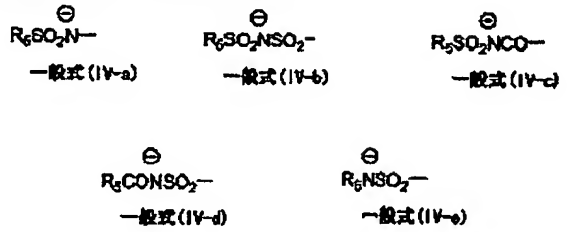
【0050】前記一般式（III－a）及び一般式（III－b）において、R_1及びR_2は．一般式（I）で説明した置換基と同義である。X_1及びX_2、は前述したカチオン部を表し．これらは同じであっても異なってもよい。L_1及びL_2は、アルキレン基を含んだ2価連結基を表す。Y_1及びY_2は、前述したアニオン部を表す。Y_1

とY₂は、同じであっても異なってもよい。R₁は、置換若しくは無置換のアルキル基を表す。nは3以上の数を表す。前記一般式（ＩＩＩ－ａ）及び前記一般式（ＩＩＩ－ｂ）において、R₁及びR₂としては、置換若しくは無置換のアルキル基が好ましい。L₁及びL₂としては、炭素数2以上のアルキレン基又はアルキレンオキシ基が＊

＊好ましい。Y₁及びY₂はとしては、一般式（ＩＶ－ａ）から一般式（ＩＶ－ｅ）で表されるアニオン部が好ましい。

【００５１】

【化１３】



【００５２】一般式（Ｉ－Ｖａ）から一般式（ＩＶ－ｅ）におけるR₅は、置換若しくは無置換の、アルキル基、アリール基又は複素環基を表す。

【００５３】R₅のアルキル基、アリール基及び複素環基としては、前記一般式（Ｉ）のR₁で詳述したものが好ましく用いられる。中でも、前記一般式（ＩＶ－ａ）から前記一般式（ＩＶ－ｃ）の場合には、フッ素置換アルキル基が好ましく、トリフルオロメチル基及びペンタフルオロエチル基がさらに好ましい。前記一般式（ＩＶ－ｄ）の場合には、C数１～５のフッ素置換アルキル基、及び置換若しくは無置換フェニル基が好ましい。前記一般式（ＩＶ－ｅ）の場合には、置換若しくは無置換のフェニル基が好ましい。

【００５４】前記一般式（ＩＩＩ－ａ）及び前記一般式（ＩＩＩ－ｂ）において、nは3から３０が好ましく、6から２０がより好ましい。

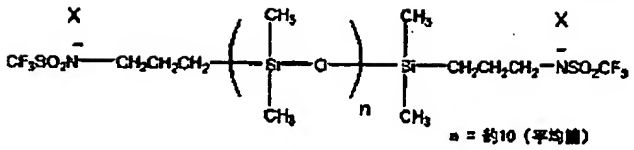
【００５５】本発明の塩として特に好ましい構造は、以下の通りである。即ち、前記一般式（ＩＩＩ－ａ）又は前記一般式（ＩＩＩ－ｂ）において、前記R₁及びR₂が炭素原子数１～３のアルキル基であり、前記X₁及びX₂がリチウムイオンであり、前記L₁及びL₂が各々独立に－（CH₂）₂－及び－（CH₂）₂OCH₂CH₂－のいずれかで表される２価連結基であり、Y₁及びY₂が各々独立に前記一般式（ＩＶ－ａ）及び前記一般式（ＩＶ－ｂ）のいずれかの構造で表されるアニオン部を含む置換基である構造で表される塩である。前記一般式（ＩＶ－ａ）及び一般式（ＩＶ－ｂ）において、R₅は炭素原子数１～３のアルキル基を表す。

【００５６】以下に本発明の電解質組成物に用いる塩のアニオン構造、カチオン構造、及びそれらを組合せた塩の具体例を示すが、それらは任意に組合せることができ、本発明はこれに限定されるわけではない。

【００５７】

【化１４】

15 16

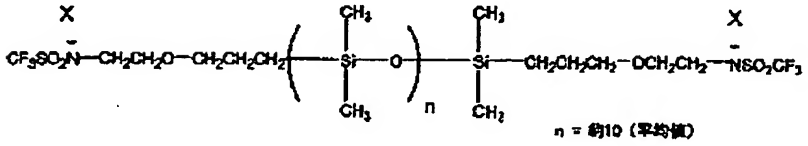


(P-1) X = Li^+

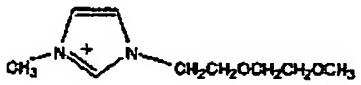
(P-2) X = 

(P-3) X = 

(P-4) X = $CH_3\overset{+}{N}(CH_2CH_3)_3$



(P-5) X = Li^+

(P-6) X = 

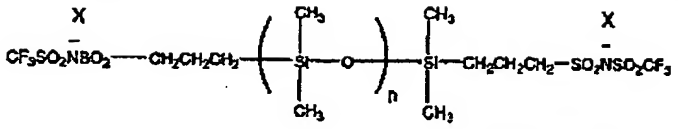
(P-7) X = 

(P-8) X = $CH_3OCH_2CH_2\overset{+}{N}(CH_2CH_3)_3$

【００５８】

【化１５】

17 18



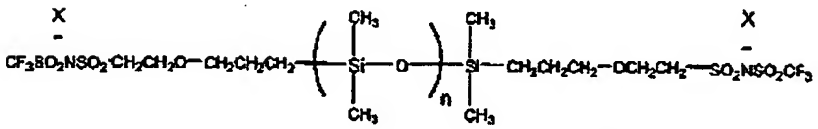
n≒約10（平均値）

(P-9) X = Li^+

(P-10) X = 

(P-11) X = 

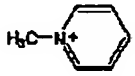
(P-12) X = $CH_3N^+(CH_2CH_3)_3$



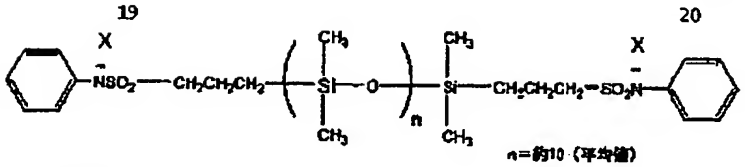
n≒約30（平均値）

(P-13) X = Li^+

(P-14) X = 

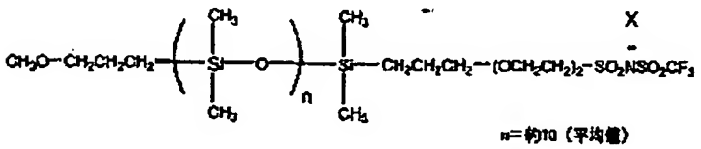
(P-15) X = 

【００５９】 【化１６】



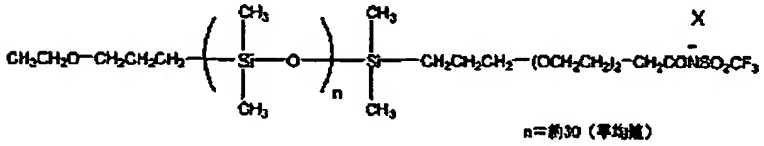
(P-16) X = Li^+

(P-17) X =



(P-18) X = Li^+

(P-19) X =



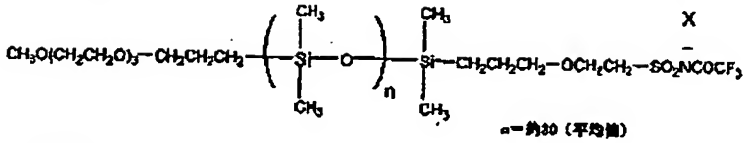
(P-20) X = Li^+

(P-21) X =

【００６０】

【化１７】

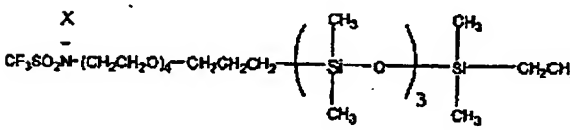
21 22



n＝約10（平均値）

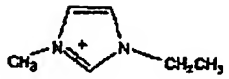
(P-22) X＝ Li^+

(P-23) X＝

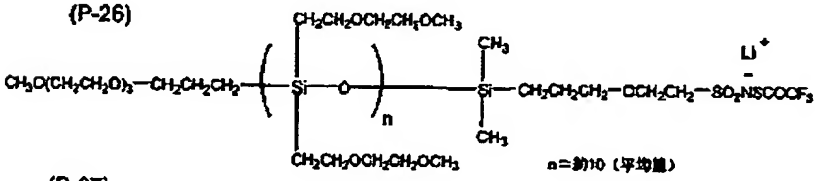


(P-24) X＝ Li^+

(P-25) X＝

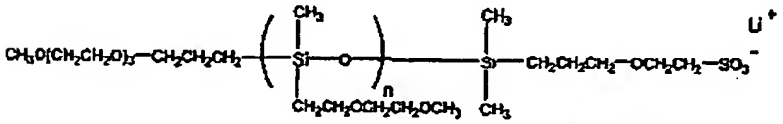


(P-26)



n＝約10（平均値）

(P-27)

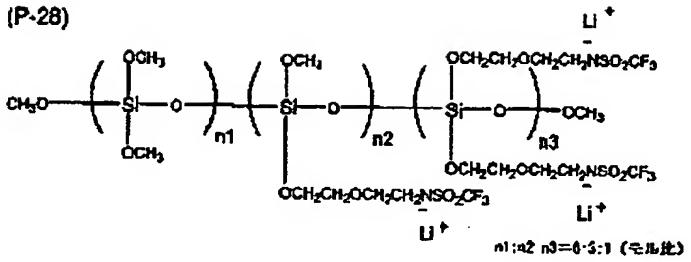


n＝約10（平均値）

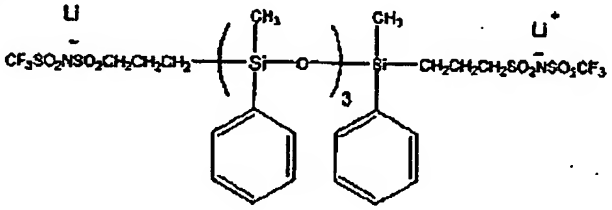
【００６１】 【化１８】

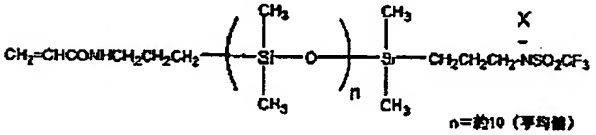
23 24

(P-28)



(P-29)

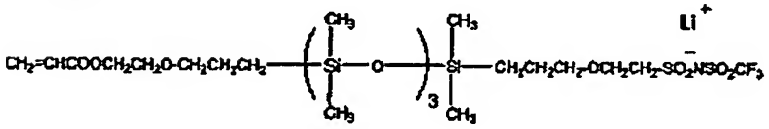




(P-30) X = Li^+

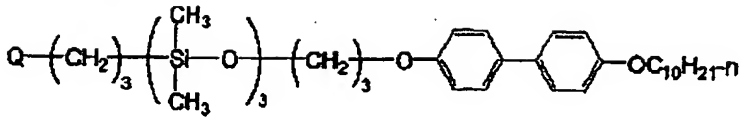
(P-31) X =

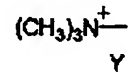
(P-32)



【００６２】

【化１９】



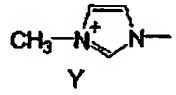
Q＝ 

(P-33) Y＝ I^-

(P-34) Y＝ $^-N(SO_2CF_3)_2$

(P-35) Y＝ BF_4^-

(P-36) Y＝ $CF_3SO_3^-$

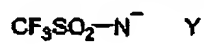
Q＝ 

(P-37) Y＝ I^-

(P-38) Y＝ $^-N(SO_2CF_3)_2$

(P-39) Y＝ BF_4^-

(P-40) Y＝ $CF_3SO_3^-$

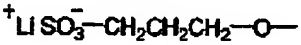
Q＝ 

(P-41) Y＝ Li^+

(P-42) Y＝ 

(P-43) Q＝

(P-44) Q＝

(P-45) Q＝ 

【００６３】本発明の電解質組成物を光電気化学電池の電解質に用いる場合、電荷キャリアとして、I^-とI_3^-を含む電解質を用いることが好ましく、それらは任意の塩の形で添加することができる。好ましい塩としては、それぞれYI^-及びYI_3^-が挙げられる。ここでYは、前記一般式（ＩＩ－ａ）、前記一般式（ＩＩ－ｂ）及び前記一般式（ＩＩ－ｃ）のいずれかで表されるカチオン部である。YI_3^-は、YI^-存在下にヨウ素（I_2）を加え、電解質組成物中で生成させることが一般的である。その際、加えたI_2と同量のYI_3^-が生成する。

【００６４】本発明の電解質組成物中、I^-の濃度は１０～９０質量％が好ましく、３０～７０質量％がより好ましい。その際、残りの成分が全て、一般式（Ｉ）で表される本発明の化合物であることが好ましい。

【００６５】I_3^-はI^-の０．１～５０モル％であることが好ましく、０．１～２０モル％であることがより好ましく、０．５～１０モル％であることがさらに好ましく、０．５～５モル％であることが最も好ましい。

【００６６】本発明の電解質組成物にはさらに別の溶融塩を含んでもよい。好ましく用いられる溶融塩は、前記一般式（ＩＩ－ａ）、前記一般式（ＩＩ－ｂ）及び前記一般式（ＩＩ－ｃ）で示される有機カチオンと任意のア

ニオンを組合せたものである。アニオンとしては、ハロゲン化物イオン（Cl^-、Br^-等）、SCN^-、BF_4^-、PF_6^-、ClO_4^-、$(CF_3SO_2)_2N^-$、$(CF_3CF_2SO_2)_2N^-$、$CH_3SO_3^-$、$CF_3SO_3^-$、CF_3COO^-、Ph_4B^-、$(CF_3SO_2)_3C^-$等が好ましい例として挙げられ、SCN^-、$CF_3SO_3^-$、CF_3COO^-、$(CF_3SO_2)_2N^-$又はBF_4^-であるのがより好ましい。また、LiIなど他のヨウ素塩やCF$_3$COOLi、CF_3COONa、LiSCN、NaSCNなどのアルカリ金属塩を添加することもできる。アルカリ金属塩の添加量は、0．02～2質量%程度であるのが好ましく、0.1～1質量%がさらに好ましい。

【００６７】本発明の電解質組成物に、LiI、NaI、KI、CsI、CaI_2などの金属ヨウ化物、4級イミダゾリウム化合物のヨウ素塩、テトラアルキルアンモニウム化合物のヨウ素塩、Br_2とLiBr、NaBr、KBr、CsBr、$CaBr_2$などの金属臭化物、あるいはBr2とテトラアルキルアンモニウムブロマイド、ピリジニウムブロマイドなど4級アンモニウム化合物の臭素塩、フェロシアン酸塩－フェリシアン酸塩やフェロセン－フェリシニウムイオンなどの金属錯体、ポリ硫化ナトリウム、アルキルチオール－アルキルジスルフィドなどのイオウ化合物、ビオロゲン色素、ヒドロキノン－キノンなどを含有させて用いることもできる。含有させる場合、これらの化合物の使用量は、電解質化合物全体の３０質量%以下であることが好ましい。

【００６８】本発明の塩とともに、好ましくは最大でこの化合物と同質量まで溶媒を使用することができる。

【００６９】本発明の電解質に使用する溶媒は、粘度が低くイオン易動度を向上したり、又は誘電率が高く有効キャリアー濃度を向上したりして、優れたイオン伝導性を発現できる化合物であることが望ましい。このような溶媒としては、エチレンカーボネート、プロピレンカーボネートなどのカーボネート化合物、3－メチル－2－オキサゾリジノンなどの複素環化合物、ジオキサン、ジエチルエーテルなどのエーテル化合物、エチレングリコールジアルキルエーテル、プロピレングリコールジアルキルエーテル、ポリエチレングリコールジアルキルエーテル、ポリプロピレングリコールジアルキルエーテルなどの鎖状エーテル類、メタノール、エタノール、エチレングリコールモノアルキルエーテル、プロピレングリコールモノアルキルエーテル、ポリエチレングリコールモノアルキルエーテル、ポリプロピレングリコールモノアルキルエーテルなどのアルコール類、エチレングリコール、プロピレングリコール、ポリエチレングリコール、ポリプロピレングリコール、グリセリンなどの多価アルコール類、アセトニトリル、グルタロジニトリル、メトキシアセトニトリル、プロピオニトリル、ベンゾニトリルなどのニトリル化合物、カルボン酸エステル、リン酸エステル、ホスホン酸エステル等のエステル類、ジメチルスルフォキシド、スルフォランなど非プロトン極性物質、水などを用いることができる。この中でも、エチレンカーボネート、プロピレンカーボネートなどのカーボネート化合物、3－メチル－2－オキサゾリジノンなどの複素環化合物、アセトニトリル、グルタロジニトリル、メトキシアセトニトリル、プロピオニトリル、ベンゾニトリルなどのニトリル化合物、エステル類が特に好ましい。これらは単独で用いても２種以上を併用してもよい。

【００７０】溶媒としては、耐揮発性による耐久性向上の観点から、常圧（１気圧）における沸点が２００℃以上のものが好ましく、２５０℃以上のものがより好ましく、２７０℃以上のものがさらに好ましい。

【００７１】本発明の電解質組成物をリチウムイオン電池などの電気化学電池に用いる場合は、リチウム塩を加えた電解質組成物とする。その場合、使用されるリチウム塩のアニオンは、イミドアニオン（$(CF_3SO_2)_2N^-$、$(CF_3CF_2SO_2)_2N^-$）あるいはホウ素（Ｂ）、リン（Ｐ）及びイオウ（Ｓ）から選ばれる少なくとも１種類以上の元素を含有するフッ化物アニオン（BF_4^-、PF_6^-、$CF_3SO_3^-$、$C(CF_3SO_2)_3^-$など）であることがより好ましい。その時の塩の濃度としては、一般式（Ｉ）の化合物に対して１質量%から７０質量%が好ましく、２０質量%から５０質量%がさらに好ましい。

【００７２】（電気化学電池）本発明の電気化学電池は、本発明の前記電解物組成物を含むことを特徴とする。本発明の電気化学電池の態様としては、光電気化学電池や、非水二次電池が挙げられる。

【００７３】＜光電気化学電池＞以下に、本発明の電解質が好ましく用いられる光電気化学電池について説明する。本発明の光電気化学電池は、光電変換素子を外部回路で仕事をさせる電池用途に使用できるようにしたものであり、輻射線に感応する半導体を含む感光層と電荷移動層と対極とを有する。この電荷移動層に本発明の電解質組成物が含有されている。

【００７４】以下に、本発明の電解質組成物を利用した本発明の光電気化学電池について説明する。本発明の光電気化学電池は、前記電解質組成物を含む電荷輸送層と、色素で増感された半導体を含む感光層と、対極とを有し、いわゆる以下に説明する光電変換素子を外部回路で仕事をさせるように構成したものである。本発明の光電気化学電池は、前記電荷輸送層が本発明の電解質組成物を含有しているので、光電変換性能に優れるとともに、経時での電池性能の劣化が小さい優れた耐久性を示す。

【００７５】－光電変換素子－

図１に、本発明に適用可能な光電変換素子の一例を示す。光電変換素子１０は、導電層１２、下塗り層１４、感光層１６、電荷輸送層１８及び対極導電層２０を順次

積層してなる．感光層１６は、色素ｄによって増感した半導体層２４と．電荷輸送材料ｔとからなる。半導体層２４は、半導体微粒子ｓからなる多孔性の層であり、半導体微粒子ｓの間には空隙が形成され．該空隙に電荷輸送材料ｔが浸透している。電荷輸送材料ｔは、電荷輸送層１８に用いる材料と同じ成分からなる。導電層１２の下には基板２６．及び対極導電層２０の下には基板２８が配置されている。基板２６、２８は光電変換素子に強度を付与するためのものであり、なくてもよい。また、それぞれの層の境界、例えば、導電層１２と感光層１６との境界、感光層１６と電荷輸送層１８との境界．電荷輸送層１８と対極導電層２０との境界等では、各層の構成成分同士が相互に拡散混合していてもよい。尚．光電変換素子１０には、いずれか又は双方から光を入射してもよく、光を入射する側の導電層１２と基板２６及び／又は対極導電層２０と基板２８を、それぞれ光透過性を有する材料から構成することができる。

【００７６】次に、光電変換素子１０の作用について説明する。尚、半導体微粒子ｓがｎ型である場合について説明する。光電変換素子１０に光が入射すると．入射した光は感光層１６に達し．色素ｄ等によって吸収され、励起状態の色素ｄを生成する。励起された色素ｄ等は、高エネルギーの電子を半導体微粒子ｓの伝導帯に渡し、自らは酸化体となる。前記伝導帯に移った電子は半導体微粒子ｓのネットワークにより導電層１２に到達する。従って、導電層１２は対極導電層２０に対して負の電位を持つ。光電変換素子１０を光電池に利用した態様では．この光電池を外部回路につなぐと．導電層１２中の電子は外部回路で仕事をしながら対極導電層２０に達する。電子は、電荷輸送材料が電解質である場合は．この電解質成分（例えばI^-）を還元するとともに、生成した還元体（例えばI_3^-）が色素ｄの酸化体を還元して元に戻す。光を照射し続けることにより．一連の反応が引き続き起こり．電気を取り出すことができる。

【００７７】以下、前記光電変換素子の各層に使用可能な材料及びその形成方法について説明する。尚．以下で「導電性支持体」というときは、導電層１２のみ．及び導電層１２と任意で設ける基板２６からなるものの双方を含み、「対極」というときは、対極導電層２０のみ、及び対極導電層２０と任意で設ける基板２６からなるものの双方を含む。

【００７８】（Ａ）導電性支持体

導電性支持体は．（１）導電層の単層．又は（２）導電層及び基板の２層からなる。（１）の場合は、導電層として強度や密封性が十分に保たれるような材料が使用される。例えば．金属材料（白金、金．銀、銅、亜鉛、チタン．アルミニウム等又はこれらを含む合金）を用いることができる。（２）の場合、感光層側に導電剤を含む導電層を有する基板を使用することができる。好ましい導電剤としては．金属（例えば白金．金、銀、銅．亜鉛．チタン、アルミニウム．インジウム等又はこれらを含む合金）、炭素、又は導電性金属酸化物（インジウムースズ複合酸化物、酸化スズにフッ素又はアンチモンをドープしたもの等）が挙げられる。導電層の厚さは、０．０２～１０μｍ程度が好ましい。

【００７９】導電性支持体は、表面抵抗が低い程よい。表面抵抗の範囲は、５０Ω／□以下が好ましく．２０Ω／□以下がより好ましい。

【００８０】導電性支持体側から光を照射する場合には．導電性支持体は実質的に透明であるのが好ましい。実質的に透明であるとは．可視～近赤外領域（４００～１２００ｎｍ）の光の一部又は全域において透過率が１０％以上であることを意味し、５０％以上であるのが好ましく、８０％以上がより好ましい。特に、感光層が感度を有する波長域の透過率が高いことが好ましい。

【００８１】透明導電性支持体としては、ガラス又はプラスチック等の透明基板の表面に導電性金属酸化物からなる透明導電層を塗布又は蒸着等により形成したものが好ましい。透明導電層としては、フッ素若しくはアンチモンをドーピングした二酸化スズあるいはインジウムースズ酸化物（ＩＴＯ）が好ましい。透明基板には．低コストと強度の点で有利なソーダガラス．アルカリ溶出の影響のない無アルカリガラスなどのガラス基板のほか、透明ポリマーフィルムを用いることができる。透明ポリマーフィルムの材料としては、トリアセチルセルロース（ＴＡＣ）、ポリエチレンテレフタレート（ＰＥＴ）、ポリエチレンナフタレート（ＰＥＮ）．シンジオタクチックポリスチレン（ＳＰＳ）、ポリフェニレンスルフィド（ＰＰＳ）．ポリカーボネート（ＰＣ）、ポリアリレート（ＰＡｒ）．ポリスルフォン（ＰＳＦ）、ポリエステルスルフォン（ＰＥＳ）．ポリイミド（ＰＩ）．ポリエーテルイミド（ＰＥＩ）．環状ポリオレフィン．ブロム化フェノキシ等がある。十分な透明性を確保するために．導電性金属酸化物の塗布量はガラス又はプラスチックの支持体１ｍ²当たり０．０１～１００ｇとするのが好ましい。

【００８２】透明導電性支持体の抵抗を下げる目的で金属リードを用いるのが好ましい。金属リードの材質は、白金．金、ニッケル、チタン、アルミニウム、銅．銀、等の金属が好ましい。金属リードは透明基板に．蒸着、スパッタリング等で設置し．その上に導電性の酸化スズ又はＩＴＯ膜からなる透明導電層を設けるのが好ましい。金属リード設置による入射光量の低下は、好ましくは１０％以内．より好ましくは１～５％とする。

【００８３】（Ｂ）感光層

前記感光層は．光を吸収して電荷分離を行い、電子と正孔を生ずる機能を有する。前記感光層は色素増感された半導体を含む。色素増感された半導体では、光吸収及びこれによる電子及び正孔の発生は主として色素において起こり、半導体はこの電子（又は正孔）を受け取り、伝

達する役割を担う。本発明で用いる半導体は、光励起下で伝導体電子がキャリアーとなり、アノード電流を与えるｎ型半導体であることが好ましい。

【００８４】（Ｂ－１）半導体

半導体としては、シリコン、ゲルマニウムのような単体半導体、ＩＩＩ－Ｖ系化合物半導体、金属のカルコゲナイド（例えば酸化物、硫化物、セレン化物、又はそれらの複合物等）、又はペロブスカイト構造を有する化合物（例えばチタン酸ストロンチウム、チタン酸カルシウム、チタン酸ナトリウム、チタン酸バリウム、ニオブ酸カリウム等）等を使用することができる。

【００８５】好ましい金属のカルコゲナイドとしては、チタン、スズ、亜鉛、鉄、タングステン、ジルコニウム、ハフニウム、ストロンチウム、インジウム、セリウム、イットリウム、ランタン、バナジウム、ニオブ、又はタンタルの酸化物、カドミウム、亜鉛、鉛、銀、アンチモン又はビスマスの硫化物、カドミウム又は鉛のセレン化物、カドミウムのテルル化物等が挙げられる。他の化合物半導体としては、亜鉛、ガリウム、インジウム、カドミウム等のリン化物、ガリウムーヒ素又は銅－インジウムのセレン化物、銅－インジウムの硫化物等が挙げられる。さらには、M_xO_y、$M^1_xM^2_yO_z$（Ｍ、Ｍ¹及びＭ²はそれぞれ金属元素、Ｏは酸素原子、ｘ、ｙ及びｚは価数が中性になる組み合わせの数）で表される複合物も好ましく用いることができる。

【００８６】本発明に用いる半導体の具体例としては、Ｓｉ、TiO_2、SnO_2、Fe_2O_3、WO_3、ＺｎＯ、Nb_2O_5、ＣｄＳ、ＺｎＳ、ＰｂＳ、Bi_2S_3、ＣｄＳｅ、ＣｄＴｅ、$SrTiO_3$、ＧａＰ、ＩｎＰ、ＧａＡｓ、$CuInS_2$、$CuInSe_2$等が好ましく、TiO_2、ＺｎＯ、SnO_2、Fe_2O_3、WO_3、Nb_2O_5、ＣｄＳ、ＰｂＳ、ＣｄＳｅ、$SrTiO_3$、ＩｎＰ、ＧａＡｓ、$CuInS_2$又は$CuInSe_2$がより好ましく、TiO_2又はNb_2O_5が特に好ましく、TiO_2が最も好ましい。TiO_2は、アナターゼ型結晶を７０％以上含むTiO_2が好ましく、１００％アナターゼ型結晶のTiO_2が特に好ましい。また、これらの半導体中の電子電導性を上げる目的で金属をドープすることも有効である。ドープする金属としては、２価、３価の金属が好ましい。半導体から電荷輸送層へ逆電流が流れるのを防止する目的で、半導体に１価の金属をドープすることも有効である。

【００８７】本発明に用いる半導体は、単結晶でも多結晶でもよいが、製造コスト、原材料確保、エネルギーペイバックタイム等の観点から、多結晶が好ましく、半導体微粒子からなる多孔質膜が特に好ましい。また、一部アモルファス部分を含んでいてもよい。

【００８８】半導体微粒子の粒径は一般にｎｍ～μｍのオーダーである。投影面積を円に換算したときの直径から求めた一次粒子の平均粒径は、５～２００ｎｍであるのが好ましく、８～１００ｎｍがより好ましい。また分散液中の半導体微粒子（二次粒子）の平均粒径は０．０１～３０μｍが好ましい。粒径分布の異なる２種類以上の微粒子を混合してもよく、この場合小さい粒子の平均サイズは２５ｎｍ以下であるのが好ましく、より好ましくは１０ｎｍ以下である。入射光を散乱させて光捕獲率を向上させる目的で、粒径の大きな、例えば１００ｎｍ以上、３００ｎｍ程度の半導体粒子を混合することも好ましい。

【００８９】半導体微粒子の種類は、１種でもよく、異なる２種以上の混合であってもよい。２種以上の半導体微粒子を混合して使用する場合、１種は、TiO_2、ＺｎＯ、Nb_2O_5若しくは$SrTiO_3$であることが好ましい。またもう１種としては、SnO_2、Fe_2O_3、WO_3であることが好ましい。さらに好ましい組み合わせとしては、ＺｎＯとSnO_2、ＺｎＯとWO_3又はＺｎＯ、SnO_2とWO_3などの組み合わせを挙げることができる。２種以上の半導体微粒子を混合して用いる場合、それぞれの粒径が異なっていてもよい。特に、上記１種目で挙げた半導体微粒子の粒径が大きく、２種目以降で挙げた半導体微粒子が小さい組み合わせが好ましい。好ましくは、大きい粒径の粒子が１００ｎｍ以上で、小さい粒径の粒子が１５ｎｍ以下の組み合わせである。

【００９０】半導体微粒子の作製法としては、作花済夫の「ゾルーゲル法の科学」アグネ承風社（１９９８年）、技術情報協会の「ゾルーゲル法による薄膜コーティング技術」（１９９５年）等に記載のゾルーゲル法、杉本忠夫の「新合成法ゲルーゾル法による単分散粒子の合成とサイズ形態制御」、まてりあ、第３５巻、第９号、１０１２～１０１８頁（１９９６年）に記載のゲルーゾル法が好ましい。また、Ｄｅｇｕｓｓａ社が開発した塩化物を酸水素塩中で高温加水分解により酸化物を作製する方法も好ましい。

【００９１】半導体微粒子が酸化チタンの場合、上記ゾルーゲル法、ゲルーゾル法、塩化物の酸水素塩中での高温加水分解法のいずれも好ましいが、さらに清野学の「酸化チタン　物性と応用技術」技報堂出版（１９９７年）に記載の硫酸法及び塩素法を用いることもできる。さらに、ゾルーゲル法として、Ｂａｒｂｅらのジャーナル・オブ・アメリカン・セラミック・ソサエティー、第８０巻、第１２号、３１５７～３１７１頁（１９９７年）に記載の方法や、Ｂｕｒｎｓｉｄｅらのケミストリー・オブ・マテリアルズ、第１０巻、第９号、２４１９～２４２５頁に記載の方法も好ましい。

【００９２】（Ｂ－２）半導体微粒子層

前記半導体は、例えば、前記導電性支持体上に形成された半導体微粒子層の形態で使用される。半導体微粒子を導電性支持体上に塗布するには、半導体微粒子の分散液又はコロイド溶液を導電性支持体上に塗布する方法の他に、前述のゾルーゲル法等を使用することもできる。光

電変換素子の量産化、半導体微粒子液の物性、導電性支持体の融通性等を考慮した場合、湿式の製膜方法が比較的有利である。湿式の製膜方法としては、塗布法、印刷法、電解析出法及び電着法が代表的である。また、金属を酸化する方法、金属溶液から配位子交換等で液相にて析出させる方法（ＬＰＤ法）、スパッタ等で蒸着する方法、ＣＶＤ法、あるいは加温した基板上に熱分解する金属酸化物プレカーサーを吹き付けて金属酸化物を形成するＳＰＤ法を利用することもできる。

【００９３】半導体微粒子の分散液を作製する方法としては、前述のゾル－ゲル法の他に、乳鉢ですり潰す方法、ミルを使って粉砕しながら分散する方法、あるいは半導体を合成する際に溶媒中で微粒子として析出させそのまま使用する方法等が挙げられる。

【００９４】分散媒としては、水又は各種の有機溶媒（例えばメタノール、エタノール、イソプロピルアルコール、シトロネロール、ターピネオール、ジクロロメタン、アセトン、アセトニトリル、酢酸エチル等）が挙げられる。分散の際、必要に応じて、例えばポリエチレングリコール、ヒドロキシエチルセルロース、カルボキシメチルセルロースのようなポリマー、界面活性剤、酸、又はキレート剤等を分散助剤として用いてもよい。ポリエチレングリコールの分子量を変えることで、分散液の粘度が調節可能となり、さらに剥がれにくい半導体層を形成したり、半導体層の空隙率をコントロールできるので、ポリエチレングリコールを添加することは好ましい。

【００９５】塗布方法としては、アプリケーション系としてローラ法、ディップ法等、メータリング系としてエアーナイフ法、ブレード法等が好ましい。また、アプリケーションとメータリングを同一部分にできるものとして、特公昭５８－４５８９号に開示されているワイヤーバー法、米国特許２６８１２９４号、同２７６１４１９号、同２７６１７９１号等に記載のスライドホッパー法、エクストルージョン法、カーテン法等が好ましい。また、汎用機として、スピン法やスプレー法も好ましい。湿式印刷方法としては、凸版、オフセット及びグラビアの３大印刷法をはじめ、凹版、ゴム版、スクリーン印刷等が好ましい。これらの中から、液粘度やウェット厚さに応じて、好ましい製膜方法を選択する。

【００９６】半導体微粒子の層は単層に限らず、粒径の違った半導体微粒子の分散液を多層塗布したり、種類が異なる半導体微粒子（あるいは異なるバインダー、添加剤）を含有する塗布層を多層塗布したりすることもできる。一度の塗布で膜厚が不足の場合にも多層塗布は有効である。

【００９７】一般に、半導体微粒子層の厚さ（感光層の厚さと同じ）が厚くなるほど単位投影面積当たりの担持色素量が増えるため、光の捕獲率が高くなるが、生成した電子の拡散距離が増すため電荷再結合によるロスも大きくなる。したがって、半導体微粒子層の好ましい厚さは、０．１～１００μｍである。光電池に用いる場合、半導体微粒子層の厚さは１～３０μｍが好ましく、２～２５μｍがより好ましい。半導体微粒子の支持体１ｍ²当たりに対する塗布量は、０．５～１００ｇが好ましく、３～５０ｇがより好ましい。

【００９８】半導体微粒子を導電性支持体上に塗布した後で半導体微粒子同士を電子的に接触させるとともに、塗膜強度の向上や支持体との密着性を向上させるために、加熱処理するのが好ましい。加熱温度の範囲は、４０℃以上７００℃以下が好ましく、１００℃以上６００℃以下がより好ましい。また、加熱時間は１０分～１０時間程度である。ポリマーフィルムのように融点や軟化点の低い支持体を用いる場合、高温処理は支持体の劣化を招くため好ましくない。またコストの観点からもできる限り低温（例えば５０℃～３５０℃）であることが好ましい。低温化は、５ｎｍ以下の小さい半導体微粒子や鉱酸、金属酸化物プレカーサーの存在下での加熱処理等により可能となり、また、紫外線、赤外線、マイクロ波等の照射や電界、超音波を印加することにより行うこともできる。同時に不要な有機物等を除去する目的で、上記の照射や印加のほか加熱、減圧、酸素プラズマ処理、純水洗浄、溶剤洗浄、ガス洗浄等を適宜組み合わせて併用することが好ましい。

【００９９】加熱処理後、半導体微粒子の表面積を増大させたり、半導体微粒子近傍の純度を高め、色素から半導体微粒子への電子注入効率を高める目的で、例えば四塩化チタン水溶液を用いた化学メッキ処理や三塩化チタン水溶液を用いた電気化学的メッキ処理を行ってもよい。また、半導体微粒子から電荷輸送層へ逆電流が流れるのを防止する目的で、粒子表面に色素以外の電子電導性の低い有機物を吸着させることも有効である。吸着させる有機物としては疎水性基を有する物が好ましい。

【０１００】半導体微粒子層は、多くの色素を吸着することができるように大きな表面積を有することが好ましい。半導体微粒子の層を支持体上に塗布した状態での表面積は、投影面積に対して１０倍以上であるのが好ましく、１００倍以上であるのがより好ましい。この上限は特に制限はないが、通常１０００倍程度である。

【０１０１】（Ｂ－３）色素

感光層に用いる増感色素は、可視域や近赤外域に吸収を有し、半導体を増感し得る化合物なら任意に用いることができ、有機金属錯体色素、メチン色素、ポルフィリン系色素又はフタロシアニン系色素が好ましい。また、光電変換の波長域をできるだけ広くし、かつ変換効率を上げるため、二種類以上の色素を併用又は混合することができる。この場合、目的とする光源の波長域と強度分布に合わせるように、併用又は混合する色素とその割合を選ぶことができる。

【０１０２】色素としては、半導体微粒子の表面に対し

て吸着能力の有る適当な結合基（ｉｎｔｅｒｌｏｃｋｉｎｇ ｇｒｏｕｐ）を有しているのが好ましい。好ましい結合基としては、ＣＯＯＨ基、ＯＨ基、SO_3H基、－Ｐ（Ｏ）（ＯＨ）$_2$基又は－ＯＰ（Ｏ）（ＯＨ）$_2$基のような酸性基、あるいはオキシム、ジオキシム、ヒドロキシキノリン、サリチレート又はα－ケトエノレートのようなπ伝導性を有するキレート化基が挙げられる。中でも、ＣＯＯＨ基、－Ｐ（Ｏ）（ＯＨ）$_2$基又は－ＯＰ（Ｏ）（ＯＨ）$_2$基が特に好ましい。これらの基は、アルカリ金属等と塩を形成していてもよく、また分子内塩を形成していてもよい。また、ポリメチン色素の場合、メチン鎖がスクアリリウム環やクロコニウム環を形成する場合のように酸性基を含有する場合、この部分を結合基として有していてもよい。

【０１０３】以下、感光層に用いる好ましい増感色素を具体的に説明する。

（Ｂ－３－ａ）有機金属錯体色素

色素が金属錯体色素である場合、金属フタロシアニン色素、金属ポルフィリン色素又はルテニウム錯体色素が好ましく、ルテニウム錯体色素が特に好ましい。ルテニウム錯体色素としては、例えば米国特許４９２７７２１号、同４６８４５３７号、同５０８４３６５号、同５３５０６４４号、同５４６３０５７号、同５５２５４４０号等の各明細書、及び、特開平７－２４９７９０号、特表平１０－５０４５１２号、世界特許９８／５０３９３号、特開２０００－２６４８７号等の各公報に記載の錯体色素が挙げられる。

【０１０４】さらに、前記色素がルテニウム錯体色素である場合、下記一般式（Ｖ）で表されるルテニウム錯体色素が好ましい。

【０１０５】一般式（Ｖ）

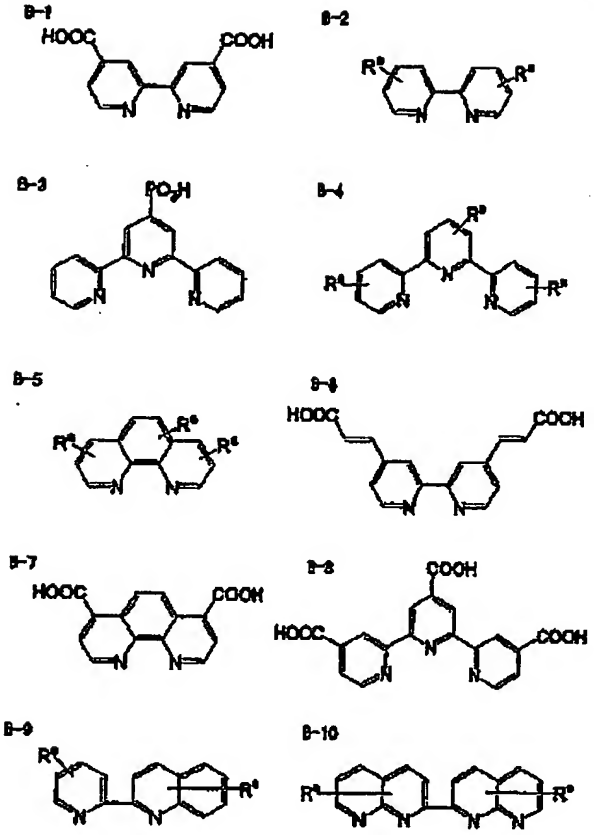
$(A^1)_t Ru(B-a)(B-b)(B-c)$

前記一般式（Ｖ）において、A^1は１又は２座の配位子を表す。A^1は、Ｃｌ、ＳＣＮ、H_2O、Ｂｒ、Ｉ、ＣＮ、ＮＣＯ、ＳｅＣＮ、β－ジケトン類、シュウ酸及びジチオカルバミン酸の誘導体からなる群から選ばれる配位子であるのが好ましい。ｔが２以上の場合、２以上のA^1は同一でも異なっていてもよい。前記一般式（Ｖ）中、Ｂ－ａ、Ｂ－ｂ及びＢ－ｃは、それぞれ独立に、下記式（Ｂ－１）～（Ｂ－１０）のいずれかで表される配位子を表す。ｔは０～３のいずれかの整数を表し、ｕ、ｖ及びｗは各々０又は１を表し、前記一般式（Ｖ）で表されるルテニウム錯体が６配位錯体となるように、配位子の種類に応じて適宜組み合わされる。

【０１０６】

【化２０】

37 38



【０１０７】前記式（Ｂ－１）～（Ｂ－１０）中、Ｒ，は、水素原子又は置換基を表し、該置換基としては、例えば、ハロゲン原子、炭素原子数１～１２の置換若しくは無置換のアルキル基、炭素原子数７～１２の置換又は無置換のアラルキル基、炭素原子数６～１２の置換若しくは無置換のアリール基、酸性基（これらの酸性基は塩を形成していてもよい）又はキレート化基が挙げられる。アルキル基及びアラルキル基のアルキル部分は直鎖状でも分岐状でもよい。また、前記アリール基及びアラルキル基のアリール部分は単環でも多環（縮合環、環集合）でもよい。前記一般式（Ｖ）中、Ｂ－ａ、Ｂ－ｂ及びＢ－ｃは同一でも異なっていてもよい。

【０１０８】有機金属錯体色素の好ましい具体例（例示化合物Ｒ－１～Ｒ－１７）を以下に示すが、本発明に用いられる色素は、以下の具体例に限定されるものではない。

【０１０９】

【化２１】

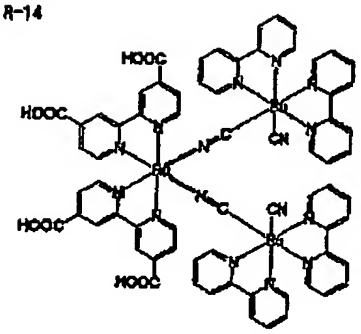
39 40

$(A^1)_pRu(B-a)(B-b)(B-c)$

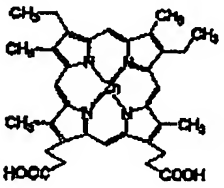
	A^1	p	B-a	B-b	B-c	R^a
R-1	SCN	2	B-1	B-1	—	—
R-2	CN	2	B-1	B-1	—	—
R-3	Cl	2	B-1	B-1	—	—
R-4	CN	2	B-7	B-7	—	—
R-5	SCN	2	B-7	B-7	—	—
R-6	SCN	2	B-1	B-2	—	H
R-7	SCN	1	B-1	B-3	—	—
R-8	Cl	1	B-1	B-4	—	H
R-9	I	2	B-1	B-5	—	H
R-10	SCN	3	B-8	—	—	—
R-11	CN	3	B-8	—	—	—
R-12	SCN	1	B-2	B-8	—	H
R-13	—	0	B-1	B-1	B-1	—

[0110] [化22]

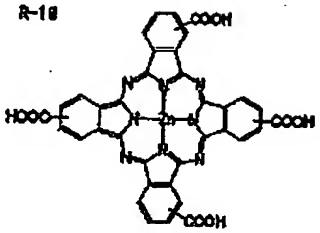
R-14



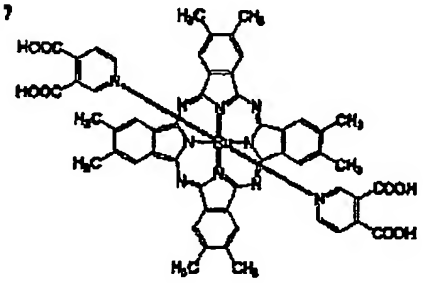
R-15



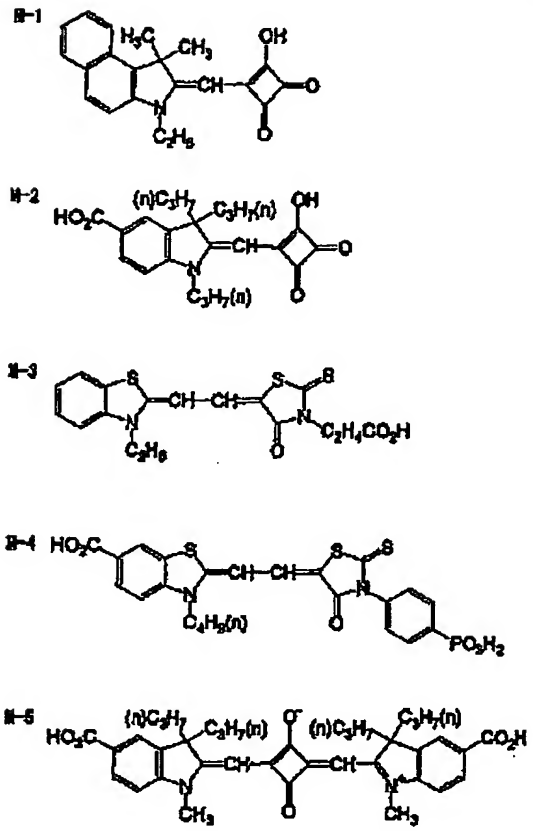
R-16



R-17

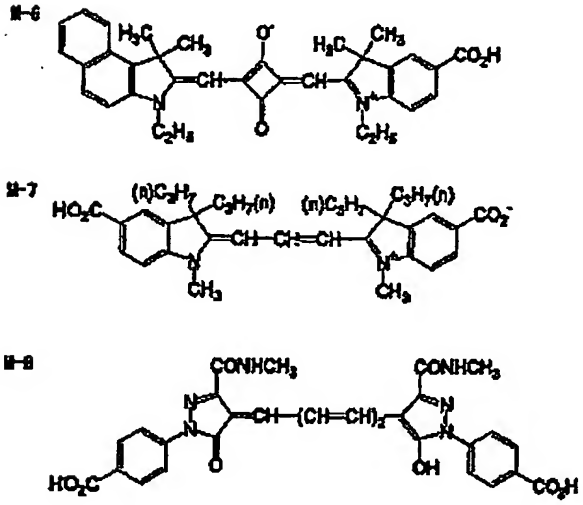


【０１１１】（Ｂ－３－ｂ）メチン色素
本発明に使用する好ましいメチン色素は、シアニン色素、メロシアニン色素、スクワリリウム色素などのポリメチン色素である。本発明で好ましく用いられるポリメチン色素としては、例えば、特開平１１－３５８３６号、特開平１１－６７２８５号、特開平１１－８６９１６号、特開平１１－９７７２５号、特開平１１－１５８３９５号、特開平１１－１６３３７８号、特開平１１－２１４７３０号、特開平１１－２１４７３１号、特開平１１－２３８９０５号、特開２０００－２６４８７号の各公報、欧州特許８９２４１１号、同９１１８４１号及び同９９１０９２号の各明細書に記載の色素が挙げられる。好ましいメチン色素の具体例を以下に示す。
【０１１２】
【化２３】



【０１１３】

＊ ＊【化２４】



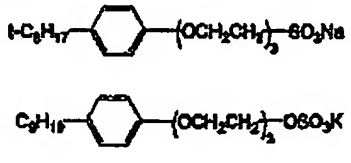
【０１１４】（Ｂ－４）半導体微粒子への色素の吸着　半導体微粒子に色素を吸着させるには、色素の溶液中に良く乾燥した半導体微粒子層を有する導電性支持体を浸漬するか、色素の溶液を半導体微粒子層に塗布する方法を用いることができる。前者の場合、浸漬法、ディップ法、ローラ法、エアーナイフ法等が使用可能である。浸

漬法の場合、色素の吸着は室温で行ってもよいし、特開平７－２４９７９０号に記載されているように加熱還流して行ってもよい。また、後者の塗布方法としては、ワイヤーバー法、スライドホッパー法、エクストルージョン法、カーテン法、スピン法、スプレー法等がある。色素を溶解する溶媒として好ましいのは、例えば、アルコール類（メタノール、エタノール、ｔ－ブタノール、ベンジルアルコール等）、ニトリル類（アセトニトリル、プロピオニトリル、３－メトキシプロピオニトリル等）、ニトロメタン、ハロゲン化炭化水素（ジクロロメタン、ジクロロエタン、クロロホルム、クロロベンゼン等）、エーテル類（ジエチルエーテル、テトラヒドロフラン等）、ジメチルスルホキシド、アミド類（Ｎ，Ｎ－ジメチルホルムアミド、Ｎ，Ｎ－ジメチルアセタミド等）、Ｎ－メチルピロリドン、１，３－ジメチルイミダゾリジノン、３－メチルオキサゾリジノン、エステル類（酢酸エチル、酢酸ブチル等）、炭酸エステル類（炭酸ジエチル、炭酸エチレン、炭酸プロピレン等）、ケトン類（アセトン、２－ブタノン、シクロヘキサノン等）、炭化水素（ヘキサン、石油エーテル、ベンゼン、トルエン等）やこれらの混合溶媒が挙げられる。

【０１１５】色素の全吸着量は、多孔質半導体電極基板の単位表面積（１ｍ²）当たり０．０１～１００ｍｍｏｌが好ましい。また色素の半導体微粒子に対する吸着量は、半導体微粒子１ｇ当たり０．０１～１ｍｍｏｌの範囲であるのが好ましい。前記範囲の色素吸着量とすることにより、半導体における増感効果が十分に得られる。これに対し、色素が少なすぎると増感効果が不十分となり、また色素が多すぎると半導体に付着していない色素が浮遊し、増感効果を低減させる原因となる。色素の吸着量を増大させるためには、吸着前に加熱処理を行うのが好ましい。加熱処理後、半導体微粒子表面に水が吸着するのを避けるため、常温に戻さずに、半導体電極基板の温度が６０～１５０℃の間で素早く色素の吸着操作を行うのが好ましい。また、色素間の凝集などの相互作用を低減する目的で、無色の化合物を色素に添加し、半導体微粒子に共吸着させてもよい。この目的で有効な化合物は界面活性な性質、構造をもった化合物であり、例えば、カルボキシル基を有する、ステロイド化合物（例えばケノデオキシコール酸）や下記の例のようなスルホン酸塩類が挙げられる。

【０１１６】

【化２５】



【０１１７】未吸着の色素は、吸着後速やかに洗浄により除去するのが好ましい。湿式洗浄槽を使い、アセトニトリル等の極性溶剤、アルコール系溶剤のような有機溶媒で洗浄を行うのが好ましい。色素を吸着した後に、アミン類や４級塩を用いて半導体微粒子の表面を処理してもよい。好ましいアミン類としては、ピリジン、４－ｔ－ブチルピリジン及びポリビニルピリジン等が挙げられる。好ましい４級塩としてはテトラブチルアンモニウムヨージド及びテトラヘキシルアンモニウムヨージド等が挙げられる。これらが液体の場合はそのまま用いてもよいし、有機溶媒に溶解して用いてもよい。

【０１１８】（Ｃ）電荷輸送層

電荷輸送層は、色素の酸化体に電子を補充する機能を有する電荷輸送材料を含有する層である。この電荷輸送層に用いることのできる代表的な電荷輸送材料の例としては、イオン輸送材料として、酸化還元対のイオンが溶解した溶液（電解液）、酸化還元対の溶液をポリマーマトリクスのゲルに含浸したいわゆるゲル電解質、酸化還元対イオンを含有する溶融塩電解質、さらには固体電解質が挙げられる。また、イオンが伴わる電荷輸送材料のほかに、本発明では、この電荷輸送層に本発明の電解質組成物を使用するが、これ以外の上記電荷輸送材料を併用することもできる。

【０１１９】（Ｃ－１）電荷輸送層の形成

電荷輸送層の形成方法に関しては２通りの方法が考えられる。１つは、感光層の上に先に対極を貼り合わせておき、その間隙に液状の電荷輸送層を挟み込む方法である。もう１つは、感光層上に直接、電荷輸送層を付与する方法で、対極はその後付与することになる。

【０１２０】前者の場合、電荷輸送層の挟み込み方法として、浸漬等による毛管現象を利用する常圧プロセス、又は常圧より低い圧力にして間隙の気相を液相に置換する真空プロセスを利用できる。

【０１２１】後者の場合、湿式の電荷輸送層においては未乾燥のまま対極を付与し、エッジ部の液漏洩防止措置を施すことになる。また、ゲル電解質の場合には、湿式で塗布して重合等の方法により固体化する方法があり、その場合には、乾燥、固定化した後に対極を付与することもできる。電解液のほかゲル電解質を付与する方法としては、前述の半導体微粒子層や色素の付与と同様の方法を利用できる。

【０１２２】（Ｄ）対極

対極は、前記の導電性支持体と同様に、導電性材料からなる対極導電層の単層構造でもよいし、対極導電層と支持基板から構成されていてもよい。対極導電層に用いる導電材としては、金属（例えば、白金、金、銀、銅、アルミニウム、マグネシウム、インジウム等）、炭素、又は導電性金属酸化物（インジウムースズ複合酸化物、フッ素ドープ酸化スズ、等）が挙げられる。この中でも、白金、金、銀、銅、アルミニウム、マグネシウムを対極層として好ましく使用することができる。対極の好まし

い支持基板の例としては、ガラス又はプラスチックであり、これに上記の導電剤を塗布又は蒸着して用いる。対極導電層の厚さは特に制限されないが、３ｎｍ～１０μｍが好ましい。対極層の表面抵抗は低い程よい。好ましい表面抵抗の範囲としては、５０Ω／□以下であり、さらに好ましくは２０Ω／□以下である。

【０１２３】導電性支持体と対極のいずれか一方又は両方から光を照射してよいので、感光層に光が到達するためには、導電性支持体と対極の少なくとも一方が実質的に透明であればよい。発電効率の向上の観点からは、導電性支持体を透明にして、光を導電性支持体側から入射させるのが好ましい。この場合、対極は光を反射する性質を有するのが好ましい。このような対極としては、金属又は導電性の酸化物を蒸着したガラス又はプラスチック、あるいは金属薄膜を使用できる。

【０１２４】対極は、電荷輸送層上に直接導電材を塗布、メッキ又は蒸着（ＰＶＤ、ＣＶＤ）するか、導電層を有する基板の導電層側を貼り付ければよい。また、導電性支持体の場合と同様に、特に対極が透明の場合には、対極の抵抗を下げる目的で金属リードを用いるのが好ましい。なお、好ましい金属リードの材質及び設置方法、金属リード設置による入射光量の低下等は導電性支持体の場合と同じである。

【０１２５】（Ｅ）その他の層

対極と導電性支持体の短絡を防止するため、予め導電性支持体と感光層の間に緻密な半導体の薄膜層を下塗り層として塗設しておくことが好ましく、電荷輸送層に電子輸送材料や正孔輸送材料を用いる場合は特に有効である。下塗り層としては、TiO_2、SnO_2、Fe_2O_3、WO_3、ＺｎＯ、Nb_2O_5が好ましく、TiO_2がより好ましい。下塗り層は、例えば、Ｅｌｅｃｔｒｏｃｈｉｍ．Ａｃｔａ ４０，６４３－６５２（１９９５）に記載されているスプレーパイロリシス法の他、スパッタ法等により塗設することができる。下塗り層の膜厚は、５～１０００ｎｍ以下が好ましく、１０～５００ｎｍがより好ましい。

【０１２６】また、電極として作用する導電性支持体と対極の一方又は両方の外側表面、導電層と基板の間又は基板の中間に、保護層、反射防止層等の機能性層を設けてもよい。これらの機能性層の形成には、その付質に応じて塗布法、蒸着法、貼り付け法等を用いることができる。

【０１２７】本発明の光電気化学電池は、前記した各々の構成物の劣化や内容物の揮散を防止するために、側面をポリマーや接着剤等で密封するのが好ましい。

【０１２８】本発明の光電気化学電池は、基本的に前記光電変換素子と同様の構成であり、前記光電変換素子をリード線等を介して外部回路に接続し、外部回路で仕事をさせるように構成したものである。前記導電性支持体及び前記対極にリード線等を介して接続される外部回路

自体は、公知のものを使用できる。また、本発明の光電気化学電池は、従来の太陽電池モジュールと基本的には同様のモジュール構造をとり得る。前記太陽電池モジュールは、一般的には金属、セラミック等の支持基板の上にセルが構成され、その上を充填樹脂や保護ガラス等で覆い、支持基板の反対側から光を取り込む構造をとるが、支持基板に強化ガラス等の透明材料を用い、その上にセルを構成してその透明の支持基板側から光を取り込む構造とすることも可能である。具体的には、スーパーストレートタイプ、サブストレートタイプ、ポッティングタイプと呼ばれるモジュール構造、アモルファスシリコン太陽電池などで用いられる基板一体型モジュール構造等が知られており、本発明の光電気化学電池も使用目的や使用場所及び環境により、適宜これらのモジュール構造を選択できる。具体的には、特開２０００－２６８８９２号の明細書に記載の構造や態様を適用することが好ましい。

【０１２９】＜非水二次電池＞以下に、本発明の電解質組成物を利用した本発明の非水二次電池について説明する。本発明の非水二次電池は、本発明の電解質組成物を含むことを特徴とする。本発明の非水二次電池は、本発明の電解質組成物を含有しているので、容量を大きく低下させることなく、優れたサイクル性を示す。

【０１３０】－正極活性物質－

本発明の電解質組成物を非水二次電池に用いる場合、正極活物質は、可逆的にリチウムイオンを挿入・放出できる遷移金属酸化物でもよいが、特にリチウム含有遷移金属酸化物が好ましい。

【０１３１】本発明において、正極活性物質として好ましく用いられるリチウム含有遷移金属酸化物正極活物質としては、リチウム含有Ｔｉ、Ｖ、Ｃｒ、Ｍｎ、Ｆｅ、Ｃｏ、Ｎｉ、Ｃｕ、Ｍｏ、Ｗを含む酸化物が好適に挙げられる。また、リチウム以外のアルカリ金属（周期律表の第１（ＩＡ）族、第２（ＩＩＡ）族の元素）、及び／又はＡｌ、Ｇａ、Ｉｎ、Ｇｅ、Ｓｎ、Ｐｂ、Ｓｂ、Ｂｉ、Ｓｉ、Ｐ、Ｂなどを混合してもよい。混合量は遷移金属に対して０～３０ｍｏｌ％が好ましい。

【０１３２】前記正極活性物質として好ましく用いられるリチウム含有遷移金属酸化物質の中でも、リチウム化合物／遷移金属化合物（ここで遷移金属とは、Ｔｉ、Ｖ、Ｃｒ、Ｍｎ、Ｆｅ、Ｃｏ、Ｎｉ、Ｍｏ、Ｗから選ばれる少なくとも１種）の合計のモル比が０．３～２．２になるように混合して合成されたものが、より好ましい。

【０１３３】また、前記リチウム化合物／遷移金属化合物の中でも、リチウム化合物／遷移金属化合物（ここで遷移金属とは、Ｖ、Ｃｒ、Ｍｎ、Ｆｅ、Ｃｏ、Ｎｉから選ばれる少なくとも１種）の合計のモル比が０．３～２．２になるように混合して合成されたものが、特に好ましい。

【０１３４】さらに、前記リチウム化合物／遷移金属化合物の中でも、$Li_gM'O_2$（M'はCo、Ni、Fe及びMnから選ばれる１種以上、g＝０～１．２）を含む材料．又は$Li_gM'_2O_4$（M'はMn、h＝０～２）で表されるスピネル構造を有する材料が．特に好ましい。前記M'及びM'としては．遷移金属以外にＡｌ．Ga、In．Ge、Sn、Pb．Sb、Bi．Si、P又はBなどを混合してもよい。混合量は遷移金属に対して０～３０ｍｏｌ％が好ましい。

【０１３５】前記$Li_gM'O_2$を含む材料．$Li_gM'_2O_4$で表されるスピネル構造を有する材料の中でも、Li_gCoO_2．Li_gNiO_2、Li_gMnO_2、$Li_gCo_hNi_{(1-h)}O_2$、$Li_gMn_2O_4$（ここで、h＝０．１～０．９、g＝０．０２～１．２、j＝０．１～０．９）が．最も好ましい。ここで．上記のg値は、充放電開始前の値であり．充放電により増減する。

【０１３６】前記正極活物質は、リチウム化合物と遷移金属化合物を混合．焼成する方法や溶液反応など．公知の方法により合成することができるが．特に焼成法が好ましい。

【０１３７】本発明の非水二次電池において用られる前記正極活物質の平均粒子サイズは、特に限定されないが．０．１～５０μｍが好ましい。比表面積としては特に限定されないが、ＢＥＴ法で０．０１～５０m^2／ｇが好ましい。また、正極活物質５ｇを蒸留水１００ｍｌに溶かした時の上澄み液のｐＨとしては、７以上１２以下が好ましい。

【０１３８】前記正極活物質を所定の粒子サイズにするには．良く知られた粉砕機や分級機を用いられる。例えば．乳鉢、ボールミル、振動ボールミル、振動ミル、遊星ボールミル、遊星ボールミル、旋回気流型ジェットミルや篩などが用いられる。前記焼成法によって得られた正極活物質は．水、酸性水溶液、アルカリ性水溶液、有機溶剤にて洗浄した後使用してもよい。

【０１３９】－負極活性物質－

本発明の非水二次電池において、負極活物質の一つとしては．リチウムの吸蔵放出が可能な炭素質材料が好適に挙げられる。前記炭素質材料とは、実質的に炭素からなる材料である。例えば、石油ピッチ．天然黒鉛．気相成長黒鉛等の人造黒鉛、及びＰＡＮ系の樹脂やフルフリルアルコール樹脂等の各種の合成樹脂を焼成した炭素質材料を挙げることができる。さらに、ＰＡＮ系炭素繊維、セルロース系炭素繊維、ピッチ系炭素繊維、気相成長炭素繊維、脱水ＰＶＡ系炭素繊維、リグニン炭素繊維、ガラス状炭素繊維．活性炭素繊維等の各種炭素繊維類、メソフェーズ微小球体、グラファイトウィスカー．平板状の黒鉛等を挙げることもできる。

【０１４０】これらの炭素質材料は．黒鉛化の程度により難黒鉛化炭素材料と黒鉛系炭素材料に分けることもできる。また、炭素質材料は．特開昭６２－２２０６６号公報．特開平２－６８５６号公報、同３－４５４７３号公報に記載される面間隔や密度、結晶子の大きさを有することが好ましい。炭素質材料は、単一の材料である必要はなく、特開平５－９０８４４号公報記載の天然黒鉛と人造黒鉛の混合物、特開平６－４５１６号公報記載の被覆層を有する黒鉛等を用いることもできる。

【０１４１】本発明の非水二次電池において、用いられるもう一つの負極活物質としては、酸化物、及び／又はカルコゲナイドが好適に挙げられる。

【０１４２】その中でも．特に、非晶質酸化物．及び／又はカルコゲナイドが好ましい。ここでいう「非晶質」とは．ＣｕＫα線を用いたＸ線回折法で２θ値で２０°から４０°の領域に頂点を有するブロードな散乱帯を有する物であり．結晶性の回折線を有してもよい．２θ値で４０°以上７０°以下に見られる結晶性の回折線の内最も強い強度が．２θ値で２０°以上４０°以下に見られるブロードな散乱帯の頂点の回折線強度の１００倍以下であるのが好ましく、５倍以下であるのがより好ましく．結晶性の回折線を有さないことが特に好ましい。

【０１４３】前記非晶質酸化物、及び／又はカルコゲナイドの中でも．半金属元素の非晶質酸化物、及び／又はカルコゲナイドがより好ましく、周期律表第１３（ＩＩＩＢ）族～１５（ＶＢ）族の元素、Ａｌ、Ga．Si、Sn．Ge、Pb、Sb．Biの単独あるいはそれらの２種以上の組み合わせからなる酸化物．カルコゲナイドが特に好ましい。

【０１４４】前記好ましい非晶質酸化物、及び／又はカルコゲナイドとしては、例えば、Ga_2O_3、SiO、GeO．SnO．SnO_2、PbO．PbO_2、Pb_2O_3、Pb_2O_4、Pb_3O_4、Sb_2O_3、Sb_2O_4、Sb_2O_5、Bi_2O_3、Bi_2O_4、$SnSiO_3$、GeS．SnS．SnS_2．PbS、PbS_2．Sb_2S_3．Sb_2S_5．$SnSiS_3$などが好ましい。また．これらは．酸化リチウムとの複合酸化物、例えば．Li_2SnO_2であってもよい。

【０１４５】本発明の非水二次電池に用いられる負極活性物質としては．前記好ましい非晶質酸化物及び／又はカルコゲナイドの中でも．Sn、Si．Geを中心とする非晶質酸化物がさらに好ましく、その中でも下記一般式（ＶＩ）で表される非晶質酸化物であることが特に好ましい。

【０１４６】一般式（ＶＩ）

$SnM^1_dM^2_eO_f$

【０１４７】前記一般式（ＶＩ）において、M^1は、Ａｌ．Ｂ、Ｐ及びGeから選ばれる少なくとも一種以上の元素．M^2は周期律表第１（ＩＡ）族元素．第２（ＩＩＡ）族元素、第３（ＩＩＩＡ）族元素及びハロゲン元素から選ばれる少なくとも一種以上の元素を表す。dは０．２以上２以下の数字．eは０．０１以上１以下の数字で０．２＜d＋e＜２．fは１以上６以下の数字を表

す。

【０１４８】以下に、Ｓｎを主体とする非晶質酸化物の具体例（Ｃ－１～Ｃ－１８）を示すが、本発明はこれらに限定されるものではない。

Ｃ－１　$SnSiO_3$

Ｃ－２　$Sn_{0.8}Al_{0.2}B_{0.4}P_{0.2}Si_{0.2}O_{3.6}$

Ｃ－３　$SnAl_{0.4}B_{0.2}Cs_{0.1}P_{0.2}O_{2.65}$

Ｃ－４　$SnAl_{0.4}B_{0.2}Mg_{0.1}P_{0.2}O_{2.7}$

Ｃ－５　$SnAl_{0.4}B_{0.4}Ba_{0.05}P_{0.4}O_{3.25}$

Ｃ－６　$SnAl_{0.4}B_{0.2}Ba_{0.05}Mg_{0.05}P_{0.4}O_{2.25}$

Ｃ－７　$SnAl_{0.4}B_{0.2}Ca_{0.1}P_{0.4}Si_{0.2}O_{3.1}$

Ｃ－８　$SnAl_{0.2}B_{0.4}Si_{0.4}O_{2.7}$

Ｃ－９　$SnAl_{0.2}B_{0.4}Mg_{0.1}P_{0.4}Si_{0.2}O_{3.6}$

Ｃ－１０　$SnAl_{0.2}B_{0.4}P_{0.2}Si_{0.2}O_{2.15}$

Ｃ－１１　$SnAl_{0.2}B_{0.4}P_{0.2}Si_{0.2}O_{1.5}$

Ｃ－１２　$SnAl_{0.4}B_{0.4}P_{0.2}Si_{0.6}O_{2.25}$

Ｃ－１３　$SnAl_{0.4}B_{0.4}Ba_{0.2}P_{0.4}Si_{0.6}O_{3.25}$

Ｃ－１４　$SnAl_{0.4}B_{0.4}Ca_{0.2}P_{0.4}Si_{0.6}O_{3.25}$

Ｃ－１５　$SnAl_{0.4}B_{0.2}Mg_{0.4}Si_{0.6}O_{2.2}$

Ｃ－１６　$SnAl_{0.4}B_{0.2}P_{0.4}Si_{0.2}O_{2.65}$

Ｃ－１７　$SnB_{0.2}K_{0.2}P_{0.2}SiO_{2.65}$

Ｃ－１８　$SnB_{0.2}F_{0.2}Mg_{0.4}P_{0.2}O_{2.65}$

【０１５０】本発明の非晶質酸化物、及び／又はカルコゲナイトは、焼成法、溶液法のいずれの方法も採用することができるが、焼成法がより好ましい。前記焼成法では、それぞれ対応する元素の酸化物、カルコゲナイトあるいは化合物をよく混合した後、焼成して非晶質酸化物及び／又はカルコゲナイトを得るのが好ましい。これらは、既に公知の方法により作製できる。

【０１５１】本発明の非水二次電池において、用いられる前記負極活性物質の平均粒子サイズは、０．１～６０μｍが好ましい。所定の粒子サイズにするには、良く知られた粉砕機や分級機が用いられる。例えば、乳鉢、ボールミル、サンドミル、振動ボールミル、遊星ボールミル、旋回気流型ジェットミルや篩などが用いられる。粉砕時には水、あるいはメタノール等の有機溶媒を共存させた湿式粉砕も必要に応じて行うことが出来る。所望の粒径とするためには、分級を行うことが好ましい。分級方法としては特に限定はなく、篩、風力分級機などを必要に応じて用いることができる。分級は、乾式、湿式ともに用いることができる。

【０１５２】本発明のＳｎ、Ｓｉ、Ｇｅを中心とする非晶質酸化物負極活性物質に併せて用いることができる負極活性物質としては、リチウムイオン又はリチウム金属を吸蔵・放出できる炭素材料や、リチウム、リチウム合金、リチウムと合金可能な金属が好適に挙げられる。

【０１５３】－電極合剤－

本発明の電極合剤としては、導電剤、結着剤やフィラーなどの他に、非プロトン性有機溶媒が添加される。

【０１５４】前記導電剤は、構成された電池において、化学変化を起こさない電子伝導性材料であれば何でもよい。通常、天然黒鉛（鱗状黒鉛、鱗片状黒鉛、土状黒鉛など）、人工黒鉛、カーボンブラック、アセチレンブラック、ケッチェンブラック、炭素繊維や金属粉（銅、ニッケル、アルミニウム、銀（特開昭６３－１４８，５５４号）など）、金属繊維あるいはポリフェニレン誘導体（特開昭５９－２０，９７１号）などの導電性材料を１種又はこれらの混合物として含ませることができる。黒鉛とアセチレンブラックの併用が特に好ましい。前記導電剤の添加量としては、１～５０質量％が好ましく、２～３０質量％がより好ましい。カーボンや黒鉛の場合は、２～１５質量％が特に好ましい。

【０１５５】本発明では電極合剤を保持するための結着剤を用いることができる。前記結着剤の例としては、多糖類、熱可塑性樹脂及びゴム弾性を有するポリマーなどが挙げられる。好ましい結着剤としては、でんぷん、カルボキシメチルセルロース、セルロース、ジアセチルセルロース、メチルセルロース、ヒドロキシエチルセルロース、ヒドロキシプロピルセルロース、アルギン酸Ｎａ、ポリアクリル酸、ポリアクリル酸Ｎａ、ポリビニルフェノール、ポリビニルメチルエーテル、ポリビニルアルコール、ポリビニルピロリドン、ポリアクリロニトリル、ポリアクリルアミド、ポリヒドロキシ（メタ）アクリレート、スチレン－マレイン酸共重合体等の水溶性ポリマー、ポリビニルクロリド、ポリテトラフルオロエチレン、ポリフッ化ビニリデン、テトラフロロエチレン－ヘキサフロロプロピレン共重合体、ビニリデンフロライド－テトラフロロエチレン－ヘキサフロロプロピレン共重合体、ポリエチレン、ポリプロピレン、エチレン－プロピレン－ジエンターポリマー（ＥＰＤＭ）、スルホン

化ＥＰＤＭ、ポリビニルアセタール樹脂、メチルメタアクリレート、２－エチルヘキシルアクリレート等の（メタ）アクリル酸エステルを含有する（メタ）アクリル酸エステル共重合体、（メタ）アクリル酸エステル－アクリロニトリル共重合体、ビニルアセテート等のビニルエステルを含有するポリビニルエステル共重合体、スチレン－ブタジエン共重合体、アクリロニトリル－ブタジエン共重合体、ポリブタジエン、ネオプレンゴム、フッ素ゴム、ポリエチレンオキシド、ポリエステルポリウレタン樹脂、ポリエーテルポリウレタン樹脂、ポリカーボネートポリウレタン樹脂、ポリエステル樹脂、フェノール樹脂、エポキシ樹脂等のエマルジョン（ラテックス）あるいはサスペンジョンを挙げることができる。特に、ポリアクリル酸エステル系のラテックス、カルボキシメチルセルロース、ポリテトラフロロエチレン、ポリフッ化ビニリデンが挙げられる。

【０１５６】前記結着剤は、単独又は混合して用いることができる。結着剤の添加量が少ないと電極合剤の保持力・凝集力が弱い。多すぎると電極体積が増加し、電極単位体積あるいは単位質量あたりの容量が減少する。このような理由から、結着剤の添加量は１～３０質量％が好ましく、特に２～１０質量％が好ましい。

【０１５７】前記フィラーは、構成された電池において化学変化を起こさない繊維状材料であれば何でも用いることができる。通常、ポリプロピレン、ポリエチレンなどのオレフィン系ポリマー、ガラス、炭素などの繊維が用いられる。フィラーの添加量は特に限定されないが、０～３０質量％が好ましい。

【０１５８】－セパレーター－

本発明の電解質組成物は、安全性確保のためにセパレーターと併用して使用することが可能である。安全性確保のため併用されるセパレーターは８０℃以上で上記の隙間を閉塞して抵抗を上げ、電流を遮断する機能を持つことが必要であり、閉塞温度が９０℃以上、１８０℃以下であることが好ましい。

【０１５９】前記セパレーターの孔の形状は通常円形や楕円形で、大きさは０．０５μｍから３０μｍであり、０．１μｍから２０μｍが好ましい。さらに、延伸法、相分離法で作った場合のように、棒状や不定形の孔であってもよい。これらの隙間の占める比率すなわち気孔率は、２０％から９０％であり、３５％から８０％が好ましい。

【０１６０】前記セパレーターは、ポリエチレン、ポリプロピレンなどの単一の材料であっても、２種以上の複合化材料であってもよい。孔径、気孔率や孔の閉塞温度などを変えた２種以上の微多孔フィルムを積層したものが、特に好ましい。

【０１６１】－集電体－

正・負極の集電体としては、構成された電池において化学変化を起こさない電子伝導体が用いられる。

【０１６２】正極の集電体としては、アルミニウム、ステンレス鋼、ニッケル、チタンなどの他に、アルミニウムやステンレス鋼の表面にカーボン、ニッケル、チタンあるいは銀を処理させたものが好ましく、アルミニウム、アルミニウム合金がより好ましい。

【０１６３】負極の集電体としては、銅、ステンレス鋼、ニッケル、チタンが好ましく、銅あるいは銅合金が特に好ましい。

【０１６４】前記集電体の形状は、通常フィルムシート状のものが使用されるが、ネット、パンチされたもの、ラス体、多孔質体、発泡体、繊維群の成形体なども用いることができる。前記集電体の厚みは、特に限定されないが、１～５００μｍが好ましい。また、集電体表面は、表面処理により凹凸を付けることも好ましい。

【０１６５】－非水二次電池の作成－

以下に、本発明の非水二次電池の作成について説明する。本発明の非水二次電池の形状としては、シート、角、シリンダーなどいずれにも適用できる。正極活物質や負極材料の合剤は、集電体の上に塗布（コート）、乾燥、圧縮されて、主に用いられる。

【０１６６】前記合剤の塗布方法としては、例えば、リバースロール法、ダイレクトロール法、ブレード法、ナイフ法、エクストルージョン法、カーテン法、グラビア法、バー法、ディップ法及びスクイーズ法を挙げることができる。その中でもブレード法、ナイフ法及びエクストルージョン法が好ましい。また、塗布は、０．１～１００ｍ／分の速度で実施されることが好ましい。この際、合剤の溶液物性、乾燥性に合わせて、上記塗布方法を選定することにより、良好な塗布層の表面状態を得ることができる。塗布は、片面ずつ逐時でも両面同時に行ってもよい。

【０１６７】さらに、前記塗布は、連続でも間欠でもストライプでもよい。その塗布層の厚み、長さや巾は、電池の形状や大きさにより決められるが、片面の塗布層の厚みは、ドライ後の圧縮された状態で、１～２０００μｍが好ましい。

【０１６８】前記電極シート塗布物の乾燥及び脱水方法は、熱風、真空、赤外線、遠赤外線、電子線及び低湿風を単独あるいは組み合わせた方法を用いることできる。乾燥温度は８０～３５０℃の範囲が好ましく、特に１００～２５０℃の範囲が好ましい。含水量は、電池全体で２０００ｐｐｍ以下が好ましく、正極合剤、負極合剤や電解質ではそれぞれ５００ｐｐｍ以下にすることが好ましい。シートのプレス法は、一般に採用されている方法を用いることができるが、特にカレンダープレス法が好ましい。プレス圧は、特に限定されないが、０．２～３ｔ／ｃｍ²が好ましい。カレンダープレス法のプレス速度は０．１～５０ｍ／分が好ましく、プレス温度は室温～２００℃が好ましい。正極シートに対する負極シート幅の比は、０．９～１．１が好ましく、０．９５～１．

０が特に好ましい。正極活物質と負極材料の含有量比は、化合物種類や合剤処方により異なる。

【０１６９】前記方法で作成された正・負の電極シートを、セパレーターを介して重ね合わせた後、そのままシート状電池に加工したり、折りまげた後角形缶に挿入し、缶とシートを電気的に接続した後、本発明の電解質組成物を注入し、封口板を用いて形成する。

【０１７０】また、正・負の電極シートをセパレーターを介して重ね合わせ巻いた後、シリンダー状缶に挿入し、缶とシートを電気的に接続した後、本発明の電解質組成物を注入し、封口板を用いてシリンダー電池を形成する。この時、安全弁を封口板として用いることができる。安全弁の他、従来から知られている種々の安全素子を備えつけてもよい。例えば、過電流防止素子として、ヒューズ、バイメタル、ＰＴＣ素子などが好適に用いられる。

【０１７１】また、安全弁のほかに電池缶の内圧上昇の対策として、電池缶に切込を入れる方法、ガスケット亀裂方法あるいは封口板亀裂方法あるいはリード板との切断方法を利用することができる。また、充電器に過充電や過放電対策を組み込んだ保護回路を具備させるか、あるいは独立に接続させてもよい。

【０１７２】また、過充電対策として、電池内圧の上昇により電流を遮断する方式を具備することができる。このとき、内圧を上げる化合物を合剤あるいは電解質に含ませることができる。内圧を上げるために用いられる化合物の例としては、Li_2CO_3、$LiHCO_3$、Na_2CO_3、$NaHCO_3$、$CaCO_3$、$MgCO_3$などの炭酸塩などを挙げることができる。

【０１７３】缶やリード板としては、電気伝導性をもつ金属や合金を用いることができる。例えば、鉄、ニッケル、チタン、クロム、モリブデン、銅、アルミニウムなど＊の金属あるいはそれらの合金が好適に用いられる。

【０１７４】キャップ、缶、シート、リード板の溶接法としては、公知の方法（例、直流又は交流の電気溶接、レーザー溶接、超音波溶接）を用いることができる。封口用シール剤としては、アスファルトなどの従来から知られている化合物や混合物を用いることができる。

【０１７５】本発明の非水二次電池の用途は、特に限定されないが、例えば、電子機器に搭載する場合、ノートパソコン、ペン入力パソコン、モバイルパソコン、電子ブックプレーヤー、携帯電話、コードレスフォン子機、ページャー、ハンディーターミナル、携帯ファックス、携帯コピー、携帯プリンター、ヘッドフォンステレオ、ビデオムービー、液晶テレビ、ハンディークリーナー、ポータブルＣＤ、ミニディスク、電気シェーバー、トランシーバー、電子手帳、電卓、メモリーカード、携帯テープレコーダー、ラジオ、バックアップ電源、メモリーカードなどが挙げられる。その他民生用として、自動車、電動車両、モーター、照明器具、玩具、ゲーム機器、ロードコンディショナー、時計、ストロボ、カメラ、医療機器（ペースメーカー、補聴器、肩もみ機など）などが挙げられる。さらに、各種軍需用、宇宙用として用いることができる。また、太陽電池と組み合わせることもできる。

【０１７６】

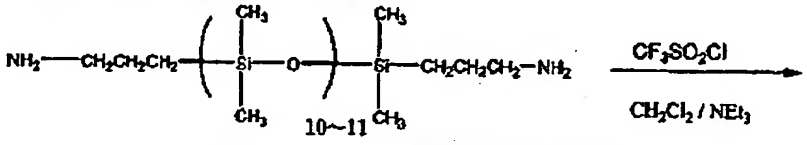
【実施例】以下、本発明を実施例によって具体的に説明するが、本発明はこれらの実施例によって、何ら限定されるものではない。

【０１７７】（実施例１）　化合物の合成

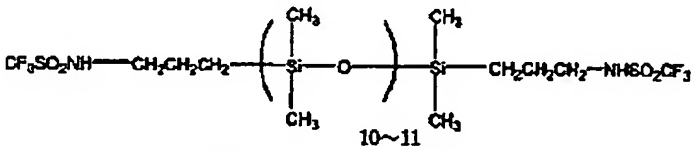
（１）例示化合物Ｐ－１及びＰ－２の合成

【０１７８】

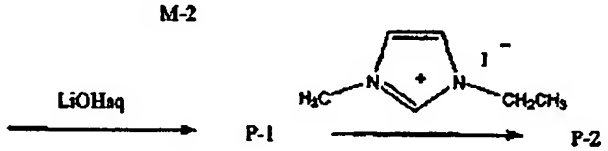
【化２６】



M-1　　平均分子量９００－１０００



M-2



【０１７９】①　中間体Ｍ－２の合成

ジアミン（Ｍ－１）１８ｇを塩化メチレン５０ｍｌに溶

解し．トリフルオロスルホニルクロリド８．４ｇを添加した後、－３０℃にて、トリエチルアミン７ｍｌを約１０分間かけて滴下した。室温下、３時間撹拌した後、反応液に水３０ｍｌを加え．塩化メチレン相を分液．１Ｎ塩酸水で洗浄し．硫酸マグネシウムで乾燥後、塩化メチレンを減圧留去した。濃縮物をシリカゲルカラムクロマト（塩化メチレン）にて精製し、１０ｇのＭ－２を油状物として得た。

【０１８０】② Ｐ－１の合成

上記で得た、ジスルホンアミド（Ｍ－２）１０ｇをＴＨＦ５０ｍｌに溶解し、ＬｉＯＨ・H_2O０．７ｇ／水５ｍｌを加え、３０分間加熱還流した。反応液に硫酸マグネシウムを加え．ろ過し．ろ液を減圧留去後、塩化メチレンを加え、不溶物をろ過したろ液を再び減圧留去し、真空乾燥機で乾燥後、６．０ｇのＰ－１を無色油状物として得た。構造確認はH^1ＮＭＲで行い、Ｓｉ上のメチル基と$CH_2CH_2CH_2$のプロトン比より．ｎの平均値１０であることがわかった（平均分子量１１９２）。

【０１８１】③ Ｐ－２の合成

ビスリチウムイミド塩（Ｐ－１）５．０ｇを塩化メチレン２０ｍｌ／水２０ｍｌに分散し、ヨウ化１－エチル－４－メチルイミダゾリウム２．０ｇを加え、室温化３０分間撹拌した。塩化メチレン相を分液し、水洗後．濃縮した。濃縮物をシリカゲルカラムクロマトにて精製し、５．５ｇのＰ－２を無色油状物として得た。

【０１８２】（実施例２） 光電気化学電池

２－１．二酸化チタン分散液の調製

内側をテフロン（登録商標）コーティングした内容積２００ｍｌのステンレス製ベッセルに二酸化チタン（日本アエロジル社製 Ｄｅｇｕｓｓａ Ｐ－２５）１５ｇ、水４５ｇ、分散剤（アルドリッチ社製．Ｔｒｉｔｏｎ Ｘ－１００）１ｇ、直径０．５ｍｍのジルコニアビーズ（ニッカトー社製）３０ｇを入れ、サンドグラインダーミル（アイメックス社製）を用いて１５００ｒｐｍにて２時間分散した。分散物からジルコニアビーズをろ過して除いた。この場合の二酸化チタンの平均粒径は２．５μｍであった。このときの粒径は、ＭＡＬＶＥＲＮ社製マスターサイザーにて測定したものである。

【０１８３】２－２．色素を吸着したTiO_2電極（電極Ａ）の作成

フッ素をドープした酸化スズをコーティングした導電性ガラス（旭硝子（株）製ＴＣＯガラス－Ｕを２０ｍｍ×２０ｍｍの大きさに切断加工したもの）の導電面側にガラス棒を用いて上記の分散液を塗布した。この際導電面側の一部（端から３ｍｍ）に粘着テープを張ってスペーサーとし、粘着テープが両端に来るようにガラスを並べて一度に８枚ずつ塗布した。塗布後．粘着テープを剥離し．室温で１日間風乾した。次に、このガラスを電気炉（ヤマト科学（株）製マッフル炉ＦＰ－３２型）に入れ．４５０℃にて３０分間焼成した。このガラスを取り出し冷却した後．色素Ｒ－１のエタノール溶液（３×１０－４モル／リットル）に３時間浸漬した。色素の染着したガラスを４－ｔｅｒｔ－ブチルピリジンに１５分間浸漬した後、エタノールで洗浄し自然乾燥させた。このようにして得られる感光層の厚さは１０μｍであり、半導体微粒子の塗布量は２０ｇ／m^2とした。なお、導電性ガラスの表面抵抗は約３０Ω／□であった。

【０１８４】２－３．光電気化学電池の作成

上述のようにして作成した色増感されたTiO_2電極基板（１ｃｍ×１ｃｍ）に．表１に示した本発明の化合物あるいは比較化合物を含む電解質組成物（Ｅ－１０２～Ｅ－１１０）のアセトニトリル溶液（アセトニトリルは組成物と同質量）を塗布し．６０℃．減圧下で．TiO_2電極に染み込ませながらアセトニトリルを留去した。これらの電極に．同じ大きさの白金蒸着ガラスを重ね合わせ光電気化学電池（サンプルＢ－１０２～Ｂ－１１０）を得た（表１、図２）。また、溶媒を用いた電解液（表１のＥ－１０１）は．上記と同じ色素増感されたTiO_2電極基板（２ｃｍ×２ｃｍ）に、その電極と同じ大きさの白金蒸着ガラスと重ね合わせた後、両ガラスの隙間に毛細管現象を利用して電解液を染み込ませ．光電気化学電池（サンプルＢ－１０１）を作成した。なお、重合性基を有する塩Ｐ－３１を含む電解質Ｅ－１１０を用いた電池（Ｂ－１１０）は、電解質を重合させるため．電池作成後に８０℃で１時間加熱を行った。

【０１８５】本実施例により、図２に示したとおり、導電性ガラス１（ガラス上に導電剤層２が設層されたもの）．TiO_2電極３．色素層４．電解質５．白金層６及びガラス７が順に積層された光電気化学電池が作成された。

【０１８６】

【表１】

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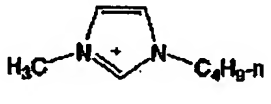
電解質	組成（質量%）	サンプル	備考
E-101	RE-1 (40) /BCE (50) /I2 (2)	B-101	比較例
E-102	RE-1 (98) /I2 (2)	B-102	比較例
E-103	RE-1 (48) /RE-2 (50) / I2 (2)	B-103	比較例
E-104	RE-1 (48) /P-2 (50) / I2 (2)	B-104	本発明
E-105	RE-1 (48) /P-3 (50) / I2 (2)	B-105	本発明
E-106	RE-1 (48) /P-6 (50) / I2 (2)	B-106	本発明
E-107	RE-1 (48) /P-19 (50) / I2 (2)	B-107	本発明
E-108	RE-1 (48) /P-14 (50) / I2 (2)	B-108	本発明
E-109	RE-1 (48) /P-21 (50) / I2 (2)	B-109	本発明
E-110	RE-1 (48) /P-31 (48) / I2 (2) /AIBN	B-110	本発明

BCE（溶媒）：ビスシアノエチルエーテル

AIBN（熱重合開始剤）：アゾイソブチロニトリル

【０１８７】

＊＊【化２７】



I^-

RE-1

$^-N(SO_2CF_3)_2$

RE-2

【０１８８】２－４．光電変換効率の測定

５００Wのキセノンランプ（ウシオ製）の光をＡＭ１．５　フィルター（Ｏｒｉｅｌ社製）及びシャープカットフィルター（ＫｅｎｋｏＬ－４１）を通すことにより紫外線を含まない模擬太陽光を発生させ．この光の強度を１００ｍＷ／ｃｍ²に調整した。

【０１８９】前述の光電気化学電池の導電性ガラスと白金蒸着ガラスに．それぞれワニ口クリップを接続し、４５℃にて、模擬太陽光を照射し、発生した電気を電流電※圧測定装置（ケースレーＳＭＵ２３８型）にて測定した。これにより求められた光電気化学電池の開放電圧（Ｖｏｃ）．短絡電流密度（Ｊｓｃ）．形状因子（ＦＦ）［＝最大出力／（開放電圧×短絡電流）］．及び変換効率（η）と恒温恒湿（６０℃、７０%Ｒ．Ｈ．）下で．４００時間経時した後の短絡電流密度の低下率を、一括して表２に記載した。

【０１９０】

【表２】

サンプル	Ｊｃｓ (mA/m²)	Voc (V)	FF	η (%)	Jsc低下率(%) 60℃－湿度70% 400時間	備考
B-101	10.1	0.66	0.64	4.3	99	比較例
B-102	7.8	0.6	0.65	3.0	11	比較例
B-103	9.2	0.64	0.68	4.0	21	比較例
B-104	11.1	0.65	0.67	4.8	5	本発明
B-105	10.6	0.64	0.68	4.6	7	本発明
B-106	10.5	0.67	0.65	4.6	8	本発明
B-107	12.1	0.64	0.64	5.0	8	本発明
B-108	10.6	0.65	0.64	4.4	6	本発明
B-109	9.9	0.64	0.68	4.3	7	本発明
B-110	9.5	0.68	0.62	4.0	4	本発明

Jsc：短絡電流密度、Voc：開放電圧、FF：形状因子、η：変換効率

【０１９１】溶媒を用いた比較電解液を用いた光電気化学電池（Ｂ－１０１）は．溶媒が揮発するため耐久性が非常に悪い。また、溶融塩ＲＥ－１及び／又はＲＥ－２を用いた比較サンプル（Ｂ－１０２．Ｂ－１０３）は経時での劣化は小さいが光電変換性能が十分ではない。それらに対して．本発明の塩を用いた時は、短絡電流密度．変換効率等の初期性能．耐久性ともに優れている。このような効果は、いずれの色素を用いた場合にも見られた。

【０１９２】（実施例３）　リチウム２次電池

３－１．正極シートの作成

正極活物質として、$LiCoO_2$を４３質量部、鱗片状黒鉛２質量部．アセチレンブラック２質量部、さらに結着剤としてポリアクリロニトリル３質量部を加え．アクリロニトリル１００質量部を媒体として混練して得られたスラリーを厚さ２０μｍのアルミニウム箔にエクストルージョン式塗布機を使って塗設し．乾燥後カレンダープレス機により圧縮成形した後、端部にアルミニウム製

のリード板を溶接し、厚さ９５μｍ．幅５４ｍｍ×長さ４９ｍｍの正極シートを作成した。

【０１９３】３－２．負極シートの作成

負極活物質として、メソフェースピッチ系炭素材料（ペトカ社）を４３質量部、導電剤としてアセチレンブラック２質量部とグラファイト２質量部の割合で混合し、さらに結着剤としてポリアクリロニトリルを３質量部を加え．Ｎ・メチルピロリドン１００質量部を媒体として混練して負極合剤スラリーを得た。負極合剤スラリーを厚さ１０μｍの銅箔にエクストルージョン式塗布機を使って塗設し、乾燥後カレンダープレス機により圧縮成形して厚さ４６μｍ．幅５５ｍｍ×長さ５０ｍｍの負極シートを作成した。負極シートの端部にニッケル製のリード板を溶接した後．露点－４０℃以下の乾燥空気中で２３０℃で１時間熱処理した。熱処理は遠赤外線ヒーターを用いて行った。

【０１９４】３－３．シート電池の作成

負極シート，正極シートはそれぞれ露点－４０℃以下の乾燥空気中で２３０℃で３０分脱水乾燥した。ドライ系＊

＊囲気中で、幅５４ｍｍ×長さ４９ｍｍの脱水乾燥済み正極シート、幅６０ｍｍ×長さ６０ｍｍに裁断したセパレータ（ポリエチレン多孔フィルム）及び不織布を積層し．不織布の上に表３に示した組成の電解質（Ｅ－２０２～２１３）を同量のアセトニトリルに溶解した液を塗布し．５０℃で減圧下、アセトニトリルを留去した。また溶媒を用いた電解液（Ｅ－２０１）は、そのままそのまま不織布に染み込ませた。その上に幅５５ｍｍ×長さ５０ｍｍの脱水乾燥済み負極シートを積層し、ポリエチレン（５０μｍ）・ポリエチレンテレフタレート（５０μｍ）のラミネートフイルムよりなる外装材を使用し４縁を真空下で熱融着して密閉し、シート型電池（Ｂ－２０１～Ｂ－２１３）を作成した。なお．重合性基を有する塩Ｐ－３０を含む電解質Ｅ－２０９を用いた電池（Ｂ－２０９）は．電解質を重合させるため、電池作成後に８０℃で１時間加熱を行った。本実施例で作成したシート電池の構成を図３に示す。

【０１９５】

【表３】

電解質番号	電解質組成（質量％）	電池番号	備考
E-201	RE-3 (30) /PC (30) /EC (40)	B-201	比較例
E-202	RE-3 (30) /RE-2 (70)	B-202	比較例
E-203	$LiBF_4$ (30) /RE-2 (70)	B-203	比較例
E-204	P-1 (100)	B-204	本発明
E-205	P-5 (100)	B-205	本発明
E-206	P-9 (100)	B-206	本発明
E-207	P-13 (100)	B-207	本発明
E-208	P-18 (100)	B-208	本発明
E-209	P-30 (98) /AIBN (2)	B-209	本発明
E-210	P-1 (30) /RE-3	B-210	本発明
E-211	P-5 (30) /RE-3	B-211	本発明
E-212	P-1 (30) /PEO	B-212	本発明
E-213	P-5 (30) /PEO	B-213	本発明

PC：プロピレンカーボネート

EC：エチレンカーボネート

RE-3：$LiN(SO_2CF_3)_2$

PEO：$-(CH_2CH_2O)_n-$（平均分子量　３０００）

【０１９６】３－４．電池性能の評価

前記方法で作成したシート型電池について、電流密度１．３ｍＡ／ｃｍ²．充電終止電圧４．２Ｖ．放電終止電圧２．６Ｖ．の条件で充放電を３０回繰り返し．３０サイクル目における放電容量を求めた。これを同一処方の５個の電池について調べ．その平均をその電池の容量とした。このようにして各々の電池の容量を求め．ＳＢ－１に対する相対容量を求めた。また．それぞれの電池について２００サイクル目の放電容量を求め、１０サイクル目の放電容量に対する比を計算しサイクル容量として表わした。それぞれの値を表４に示した。

【０１９７】

【表４】

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電池番号	相対容量	サイクル容量	備考
B-201	1	0.28	比較例
B-202	0.61	0.87	比較例
B-203	0.33	0.78	比較例
B-204	0.84	0.98	本発明
B-205	0.72	0.95	本発明
B-206	0.81	0.96	本発明
B-207	0.85	0.98	本発明
B-208	0.94	0.95	本発明
B-209	0.66	0.95	本発明
B-210	0.95	0.94	本発明
B-211	0.91	0.94	本発明
B-212	0.83	0.93	本発明
B-213	0.90	0.95	本発明

【０１９８】上記の結果より、本発明の電解質組成物は、容量の大きな低下が見られずにサイクル性を向上させていることがわかる。

【０１９９】

【発明の効果】本発明によると、実質的に揮発せず、かつ電化輸送能に優れた新規なポリシロキサン塩及び該塩を含有する新規な電解質組成物を提供し、さらに該電解質組成物を含み、耐久性とイオン伝導性に優れた電気化学電池、耐久性と光変換特性に優れた光電気化学電池、及び電池容量を低下させず、しかもサイクル特性に優れた非水二次電池を提供することを提供することができる。

【図面の簡単な説明】

【図１】　本発明の光電変換素子の一例を示す概略構成図である。

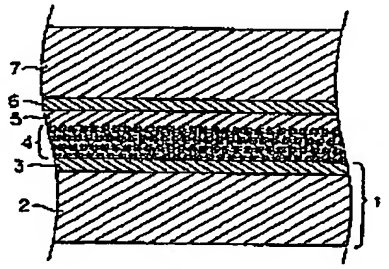
【図２】　実施例２で作成した光電気化学電池の構成を示す断面図である。

【図３】　実施例３で作成したシート型電池の構成を示す図である。

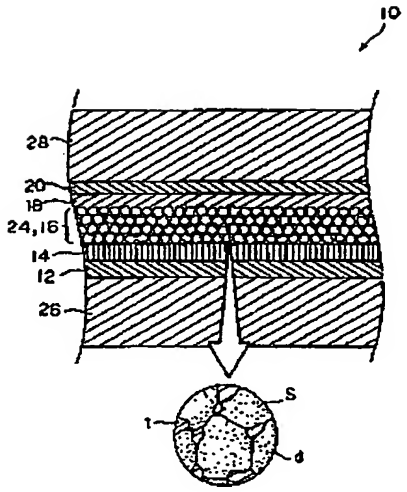
【符号の説明】

１　導電性ガラス
２　導電剤層
＊３　ＴｉO_2電極
４　色素層
５　電解質
６　白金層
７　ガラス
１０　光電変換素子
１２　導電層
１４　下塗り層
１６　感光層
１８　電荷輸送層
２０　対極導電層
２４　半導体層
２８　基板
３１　正極シート
３２　高分子固体電解質
３３　負極シート
３４　正極端子
３５　負極端子
ｓ　半導体微粒子
ｄ　色素
ｔ　電荷輸送材料

【図２】



【図1】



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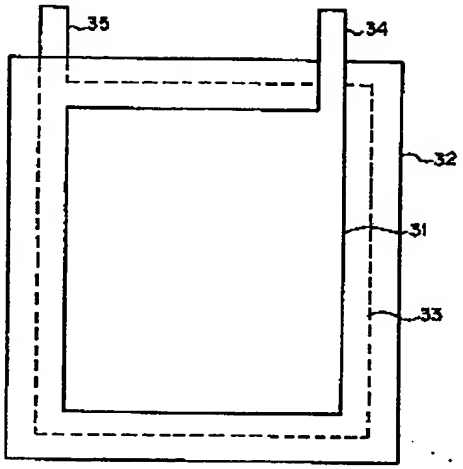

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CA26M CA27M FB02 LA02
LB20
5G301 CA30 CD01
5H029 AJ05 AK03 AL02 AL04 AL06
AL07 AL12 AM00 AM02 AM03
AM04 AM05 AM07 AM10 AM16
BJ04 BJ12 DJ09 HJ02
5H032 AA07 AS19 CC17 EE04 EE16
EE20

.NOTICES.

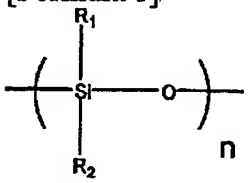
1. This document has been translated by computer.So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The electrolyte constituent characterized by containing the salt which has in structure the anion section which a proton comes to dissociate from at least one among the atomic group expressed with the following general formula (I), a sulfonamide and disulfon imide, N-acyl sulfonamide, alcohol, a phenol, and a sulfonic acid, and the cation section which is the metal ion and/or the organic cation belonging to the 1st group of a periodic table, or the 2nd group.

[Formula 1]

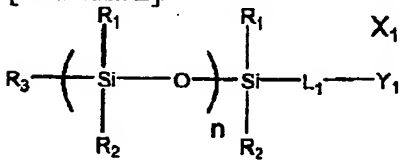


一般式（I）

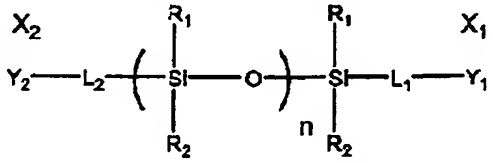
In the aforementioned general formula (I), R1 and R2 express an alkyl group, an aryl group, or an alkoxy group. n expresses three or more numbers.

[Claim 2] The electrolyte constituent according to claim 1 whose aforementioned salt is a salt expressed with the structure of either the following general formula (III-a) and the following general formula (III-b).

[Formula 2]



一般式(III-a)



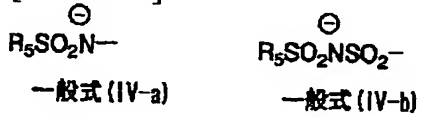
一般式(III-b)

In the aforementioned general formula (III-a) and the aforementioned general formula (III-b), R1 and R2 express an alkyl group independently respectively. X1 and X2 express the aforementioned cation section independently respectively. Even if X1 and X2 are mutually the same, they may differ. L1 and L2 express the divalent connection machine containing the alkylene machine. Y1 and Y2 express the substituent containing the aforementioned anion section. Even if Y1 and Y2 are mutually the same, they may differ. R3 expresses the alkyl group which is not replaced [substitution or]. n expresses three or more numbers.

[Claim 3] The above R1 and R2 is the alkyl groups of the carbon atomic numbers 1-3, and it is the divalent connection machine by which the above L1 and L2 is respectively expressed independently with either -(CH2) 3- and -(CH2) 3OCH2CH2-. The electrolyte constituent according to claim 1 or 2

which is a substituent containing the anion section to which Y1 and Y2 are respectively expressed with the structure of either the following general formula (IV-a) and a general formula (IV-b) independently.

[Formula 3]



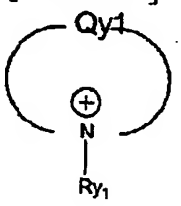
一般式(IV-a) 一般式(IV-b)

In the aforementioned general formula (IV-a) and a general formula (IV-b), R5 expresses the alkyl group of the carbon atomic numbers 1-3.

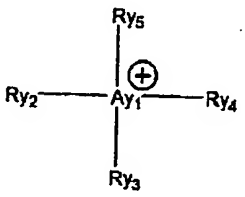
[Claim 4] An electrolyte constituent given in either of the claims 1-3 whose aforementioned cation sections are lithium ions.

[Claim 5] An electrolyte constituent given in either of the claims 1-3 whose aforementioned cation sections are either among the cation sections expressed with a general formula (II-a), a general formula (II-b), and a general formula (II-c).

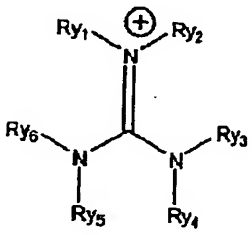
[Formula 4]



一般式(II-a)



一般式(II-b)



一般式(II-c)

In the aforementioned general formula (II-a), Qy1 expresses the atomic group which can form the aromatic cation of 5 member rings or 6 member rings with a nitrogen atom. Ry1 expresses the alkyl group or alkenyl machine which is not replaced [substitution or]. In the aforementioned general formula (II-b), Ay1 expresses a nitrogen atom or the Lynn atom. Ry1, Ry2, Ry3, and Ry4 express the alkenyl machine which is not replaced [the alkyl group which is not replaced / substitution or /, substitution, or]. Moreover, two or more may form the un-aromatic ring which connects mutually and contains Ay1 among Ry1, Ry2, Ry3, and Ry4. In the aforementioned general formula (II-c), Ry1, Ry2, Ry3, Ry4, Ry5, and Ry6 may express the alkenyl machine which is not replaced [the alkyl group which is not replaced / substitution or /, substitution, or], among those two or more may connect them mutually, and they may form a ring structure. The compound expressed with the aforementioned general formula (II-a), a general formula (II-b), and a general formula (II-c) may form a polymer through Qy1, or Ry1-Ry6.

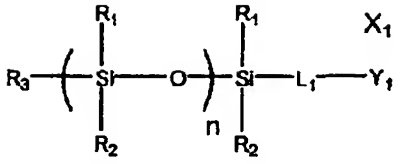
[Claim 6] The electrochemical cell characterized by including the electrolyte constituent of a publication in either of the claims 1-5.

[Claim 7] The non-water rechargeable battery characterized by including the electrolyte constituent of a publication in either of the claims 1-5.

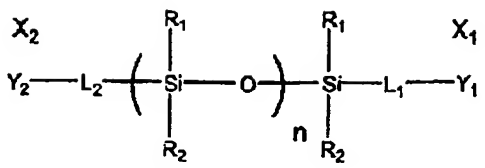
[Claim 8] The photoelectrochemical cell characterized by having the charge transfer layer which contains the electrolyte constituent of a publication in either of the claims 1-5, a photosensitive layer containing the semiconductor by which sensitization was carried out with coloring matter, and a counterelectrode.

[Claim 9] The polysiloxane salt characterized by what is expressed with the structure of either the following general formula (III-a) and the following general formula (III-b).

[Formula 5]



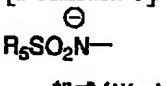
一般式(III-a)



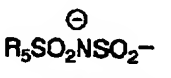
一般式(III-b)

In the aforementioned general formula (III-a) and the aforementioned general formula (III-b), R1 and R2 express the alkyl group of the carbon atomic numbers 1-3 independently respectively. X1 and X2 express a lithium ion. L1 and L2 express the binary connection machine respectively expressed with either -(CH2) 3- and -(CH2) 3OCH2CH2- independently. Y1 and Y2 express the substituent containing the anion section respectively expressed with the structure of either the following general formula (IV-a) and a general formula (IV-b) independently. R3 expresses the alkyl group which is not replaced [substitution or]. n expresses three or more numbers.

[Formula 6]



一般式(IV-a)



一般式(IV-b)

In the aforementioned general formula (IV-a) and a general formula (IV-b), R5 expresses the alkyl group of the carbon atomic numbers 1-3.

[Translation done.]

* NOTICES *

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the electrochemical cell using the electrolyte constituent which contains a cell, a new suitable as other electrochemistry device material polysiloxane salt (an "electrolyte salt" may be called below), and the salt concerned in more detail, and the electrolyte constituent concerned especially a nonaqueous electrolyte rechargeable battery, and a photoelectrochemical cell about a polysiloxane salt, an electrolyte constituent, an electrochemical cell, a non-water rechargeable battery, and a photoelectrochemical cell.
[0002]
[Description of the Prior Art] The electrolyte used for electrochemical cells, such as a non-water rechargeable battery and a coloring matter sensitization solar battery, is a medium which has the function (it is called ionic conduction) to convey the ion to inter-electrode, including the ion according to the purpose. For example, with the lithium secondary battery which is the representation of a non-water rechargeable battery, the conductivity of iodine ion and iodine trimer ion poses [transportation of a lithium ion] a problem by the coloring matter sensitization solar battery. In these cells, generally, although many solution systems with high ion conductivity are used as an electrolyte, there is a problem of an exhaustion of the solvent at the time of including in a cell and leakage reducing the endurance of a cell. That is, when the electrolyte which used the common low-molecular solvent is built into a cell, there is a problem that the cell performance by volatilization of a solvent or the liquid spill deteriorates. Moreover, in order to seal a solution in a lithium secondary battery, a metal vessel must be used, cell mass becomes heavy, and there is a problem that it is difficult to also give flexibility to a cell configuration.
[0003] In order to conquer the fault of the aforementioned solution system electrolyte, various electrolytes are proposed in recent years. although the fall of ionic conductivity does not drop a cell performance small to a solution system electrolyte, the so-called gel electrolyte which made the solution electrolyte permeate a polymer matrix has the problem obtained and said, if volatilization of a solvent cannot be inhibited completely. Moreover, although the polymer electrolyte which dissolved the salt in polymer, such as a polyethylene oxide, is expected as what solves the problem of a solution system electrolyte, it has the problem that ionic conductivity is not yet enough.
[0004] On the other hand, although the method using the so-called quality of molten salt electrolysis which used the salt of a liquid as the base at the room temperature is learned, since a low-boiling point compound is not included, while it is effective in preventing degradation of the cell performance by volatilization, since viscosity is high, generally there is a problem of a low in charge transportation ability. For example, although an opposite anion is room temperature fused salt with imidazolium salts and pyridinium salts liquefied at a room temperature, such as BF4- and 2 (CF3SO2)N-, and it is proposed as an electrolyte for lithium ion batteries, an electrolytic mechanical strength and ion conductivity conflict, and when own viscosity of fused salt was raised, or it is the means of making polymer contain etc. and a mechanical strength is strengthened, the fall of ionic

conductivity is seen. Furthermore, in the above electrolytes, ion conductivity temperature dependence is large and there is a problem that especially the ion conductivity in low temperature is inadequate.
[0005] By the way, although compound solar batteries, such as a single-crystal-silicon solar battery, a polycrystal silicon solar cell, an amorphous-silicon solar cell, a cadmium telluride, and selenium-ized indium copper, are set as the object of utilization or research and development, the photovoltaics which transform a light energy into electrical energy need to conquer troubles, such as reservation of a manufacturing cost and raw material, and the length of an energy pay back time, when making it spread. On the other hand, although many solar batteries using the organic material which pointed to large-area-izing or low-pricing are also proposed until now, a conversion efficiency is low and there is a problem that endurance is also bad.
[0006] In such a situation, the technology of a photoelectrochemical cell using the optoelectric transducer (it abbreviates to a coloring matter sensitization optoelectric transducer henceforth) using the oxide semiconductor by which sensitization was carried out to Nature (the 353rd volume, the 737-740th page, 1991), U.S. JP,4927721,B, etc. with coloring matter, and this was indicated. This cell consists of the optoelectric transducer, charge transfer layer, and counter electrode which function as a negative electrode. An optoelectric transducer consists of a conductive base material and a photosensitive layer, and a photosensitive layer contains the semiconductor with which coloring matter stuck to the front face. A charge transfer layer consists of a oxidation reduction object, and bears charge transportation between a negative electrode and a counter electrode (positive electrode). In the photoelectrochemical cell proposed by the above-mentioned patent, the solution (electrolytic solution) which uses salts, such as potassium iodide, as an electrolyte as a charge transfer layer was used. This method is cheap and it is a problem for a photoelectric conversion efficiency not to fall remarkably by evapotranspiration of the electrolytic solution and exhaustion, if it is used over a long period of time, although it is promising, or to stop functioning as a cell in that a comparatively high energy conversion efficiency (photoelectric conversion efficiency) is obtained.
[0007] The method of using as an electrolyte the imidazolium salt which is a low melting point compound as the exhaustion prevention method of the electrolytic solution at WO 95/No. 18456 is indicated to such a problem. Since according to this method water and the organic solvent which were used as an electrolytic solvent were unnecessary or little and ended conventionally, although the improvement of endurance was found, endurance is still inadequate. Moreover, when the imidazolium salt was made into high concentration, while viscosity became high, charge transportation ability fell, and there was a problem that a photoelectric conversion efficiency became low. Furthermore, there is the method of using a thoria ZORIUMU salt as an electrolyte, and there is the same problem as an imidazolium salt also in this method.
[0008] In order to conquer the fault of a solution system electrolyte also in the electrolyte used for electrochemical cells, such as a non-water rechargeable battery, the electrolytic solid state (polymer electrolyte) is studied in recent years. Although the polymer electrolyte which dissolved the salt in polymer, such as a polyethylene oxide, is expected as what solves the problem of a solution system electrolyte, ionic conductivity is not yet enough. Moreover, generally the ion transference number (in the case of a lithium secondary battery, it is the lithium ion transference number) which is one of the important electrolytic properties in the polymer electrolyte mainly reported so far is a low. therefore -- for example, the actual condition is that it is difficult to include in the goods with which a charge and discharge current decreases with time, and causes problems, such as causing the fall of capacity, and with which in the case of a lithium secondary battery it is flexible
[0009]
[Problem(s) to be Solved by the Invention] this invention solves the problem in the aforementioned former, and makes it a technical problem to attain the following purposes. Namely, this invention offers the new electrolyte constituent containing the new polysiloxane salt and this salt which did not volatilize substantially and were excellent in electrification transportation ability, does not reduce further the electrochemical cell which was excellent in endurance and ion conductivity including this

electrolyte constituent, the photoelectrochemical cell excellent in endurance and the optical transfer characteristic, and cell capacity, and aims at offering the non-water rechargeable battery which was moreover excellent in the cycle property.

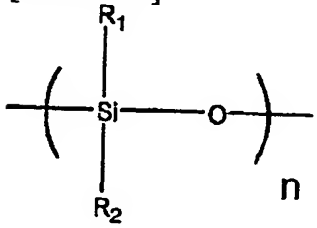
[0010]

[Means for Solving the Problem] The aforementioned The means for solving a technical problem is as follows.

<1> It is the electrolyte constituent characterized by containing the salt which has in structure the anion section which a proton comes to dissociate from at least one among the atomic group expressed with the following general formula (I), a sulfonamide and disulfon imide, N-acyl sulfonamide, alcohol, a phenol, and a sulfonic acid, and the cation section which is the metal ion and/or the organic cation belonging to the 1st group of a periodic table, or the 2nd group.

[0011]

[Formula 7]



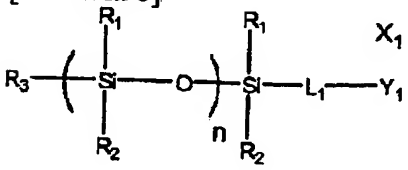
一般式（Ｉ）

[0012] In the aforementioned general formula (I), R1 and R2 express an alkyl group, an aryl group, or an alkoxy group. n expresses three or more numbers.

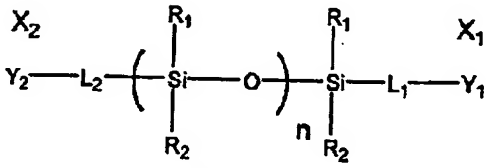
[0013] <2> The aforementioned salt is an electrolyte constituent given in the above <1> which is the salt expressed with the structure of either the following general formula (III-a) and the following general formula (III-b).

[0014]

[Formula 8]



一般式(III-a)

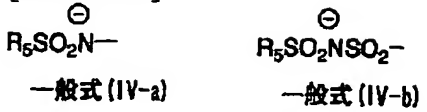


一般式(III-b)

[0015] In the aforementioned general formula (III-a) and the aforementioned general formula (III-b), R1 and R2 express an alkyl group independently respectively. X1 and X2 express the aforementioned cation section independently respectively. Even if X1 and X2 are mutually the same, they may differ. L1 and L2 express the divalent connection machine containing the alkylene machine. Y1 and Y2 express the substituent containing the aforementioned anion section. Even if Y1 and Y2 are mutually the same, they may differ. R3 expresses the alkyl group which is not replaced [substitution or]. n expresses three or more numbers.

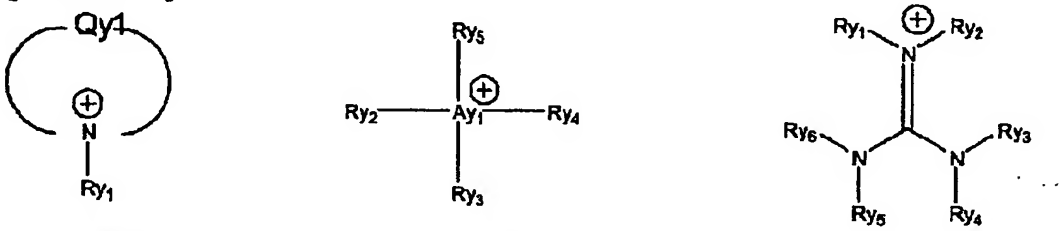
[0016] <3> The above R1 and R2 is the alkyl groups of the carbon atomic numbers 1-3. It is the divalent connection machine by which the above L1 and L2 is respectively expressed independently with either -(CH2) 3- and -(CH2) 3OCH2CH2-. Y1 and Y2 are the above <1> which is a substituent containing the anion section respectively expressed with the structure of either the following general formula (IV-a) and a general formula (IV-b) independently, or an electrolyte constituent given in <2>.

[0017]
[Formula 9]



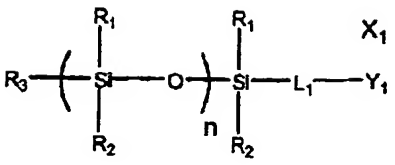
一般式(IV-a)　　一般式(IV-b)

[0018] In the aforementioned general formula (IV-a) and a general formula (IV-b), R5 expresses the alkyl group of the carbon atomic numbers 1-3.
[0019] <4> The aforementioned cation section is an electrolyte constituent given in either of <3> from the above <1> which is a lithium ion.
[0020] <5> The aforementioned cation section is an electrolyte constituent given in either of <3> from the above <1> which is either among the cation sections expressed with a general formula (II-a), a general formula (II-b), and a general formula (II-c).
[0021]
[Formula 10]

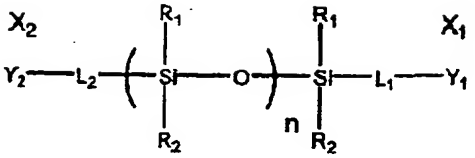


一般式(II-a)　　一般式(II-b)　　一般式(II-c)

[0022] In the aforementioned general formula (II-a), Qy1 expresses the atomic group which can form the aromatic cation of 5 member rings or 6 member rings with a nitrogen atom. Ry1 expresses the alkyl group or alkenyl machine which is not replaced [substitution or]. In the aforementioned general formula (II-b), Ay1 expresses a nitrogen atom or the Lynn atom. Ry1, Ry2, Ry3, and Ry4 express the alkenyl machine which is not replaced [the alkyl group which is not replaced / substitution or /, substitution, or]. Moreover, two or more may form the un-aromatic ring which connects mutually and contains Ay1 among Ry1, Ry2, Ry3, and Ry4. In the aforementioned general formula (II-c), Ry1, Ry2, Ry3, Ry4, Ry5, and Ry6 may express the alkenyl machine which is not replaced [the alkyl group which is not replaced / substitution or /, substitution, or], among those two or more may connect them mutually, and they may form a ring structure. The compound expressed with the aforementioned general formula (II-a), a general formula (II-b), and a general formula (II-c) may form a polymer through Qy1, or Ry1-Ry6.
[0023] <6> It is the electrochemical cell characterized by including the electrolyte constituent of a publication in either of <5> from the above <1>.
[0024] <7> It is the non-water rechargeable battery characterized by including the electrolyte constituent of a publication in either of <5> from the above <1>.
[0025] <8> It is the photoelectrochemical cell characterized by having the charge transfer layer which contains the electrolyte constituent of a publication in either of <5> from the above <1>, a photosensitive layer containing the semiconductor by which sensitization was carried out with coloring matter, and a counterelectrode.
[0026] <9> It is the polysiloxane salt characterized by what is expressed with the structure of either the following general formula (III-a) and the following general formula (III-b).
[0027]
[Formula 11]



一般式(III-a)

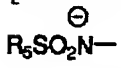


一般式(III-b)

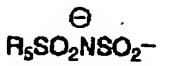
[0028] In the aforementioned general formula (III-a) and the aforementioned general formula (III-b), R1 and R2 express the alkyl group of the carbon atomic numbers 1-3 independently respectively. X1 and X2 express a lithium ion. L1 and L2 express the binary connection machine respectively expressed with either -(CH2) 3- and -(CH2) 3OCH2CH2- independently. Y1 and Y2 express the substituent containing the anion section respectively expressed with the structure of either the following general formula (IV-a) and a general formula (IV-b) independently. R3 expresses the alkyl group which is not replaced [substitution or]. n expresses three or more numbers.

[0029]

[Formula 12]



一般式(IV-a)



一般式(IV-b)

[0030] In the aforementioned general formula (IV-a) and a general formula (IV-b), R5 expresses the alkyl group of the carbon atomic numbers 1-3.

[0031]

[Embodiments of the Invention] Hereafter, the polysiloxane salt of this invention, an electrolyte constituent, an electrochemical cell, a non-water rechargeable battery, and a photoelectrochemical cell are explained. Here, the electrolyte constituent containing the polysiloxane salt and this salt of this invention is explained in detail first.

[0032] (A salt and electrolyte constituent) The electrolyte constituent of this invention is used for reaction solvents, such as a chemical reaction and metal plating, a CCD (charge-coupled device) camera, various electrochemical cells (the so-called cell), etc. It is more desirable for it to be preferably used for a non-water rechargeable battery (especially lithium secondary battery) or the photoelectrochemical cell using the following semiconductor, and to use for a photoelectrochemical cell.

[0033] The salt of this invention is characterized by having in structure the anion section which a proton comes to dissociate from at least one among the atomic group expressed with the aforementioned general formula (I), a sulfonamide and disulfon imide, N-acyl sulfonamide, alcohol, a phenol, or a sulfonic acid, and the cation section which is the metal ion and/or the organic cation belonging to the 1st group of a periodic table, or the 2nd group. The electrolyte constituent of this invention is characterized by being an electrolyte constituent containing the aforementioned salt.

[0034] The atomic group expressed with the aforementioned general formula (I) contained in the salt of a <atomic group expressed with general formula (I)> this invention is explained in full detail.

[0035] Carbon atomic numbers (Following more than C may be called) are 1-24 preferably. the aforementioned general formula (I) -- setting -- R1 and R2 -- each -- independent -- alkyl group [-- You may be branched-chain, even if it is more than C [1-10] more preferably and is a straight chain-like. For example, a methyl, ethyl, a propyl, butyl, i-propyl, i-butyl, A pentyl, a hexyl, an octyl, 2-ethylhexyl, t-octyl, A desyl, a dodecyl, tetradecyl, 2-hexyl desyl, hexadecyl, Octadecyl, cyclohexyl methyl, and octyl cyclohexyl], It is more than C [6-24] preferably, and is more than C [6-10] more preferably. aryl group [-- for example, phenyl and naphthyl] or alkoxy-group [-- more than C [1-24], for example, a methoxy, ethoxy ** butoxy, octyloxy, methoxyethoxy one, methoxy PENTA (ethyloxy), acryloyl oxyethoxy, and pentafluoro propoxy] are expressed preferably. Furthermore, these

[R1 and R2] may have the substituent. as a desirable substituent It is more than C [1-24] preferably, and is more than C [1-10] more preferably. alkyl group [which may be replaced -- You may be branched-chain even if it is a straight chain-like. For example, a methyl, ethyl, A propyl, butyl, i-propyl, i-butyl, a pentyl, a hexyl, An octyl, 2-ethylhexyl, t-octyl, a desyl, a dodecyl, Tetradecyl, 2-hexyl desyl, hexadecyl one, octadecyl, cyclohexyl methyl and octyl cyclohexyl] and the aryl group (desirable -- more than C [6-24], for example, a phenyl, --) which may be condensing the ring even if it has replaced 4-methylphenyl, 3-cyano phenyl, 2-chlorophenyl, 2-naphthyl, the heterocycle machine that may be condensing the ring even if it has replaced (the nitrogen in a ring may form 4 class at the time of a nitrogen-containing heterocycle machine.) Preferably More than C [2-24], for example, 4-pyridyl, 2-pyridyl, 1-octyl pyridinium-4-IRU, 2-pyrimidyl, 2-imidazolyl, 2-thiazolyl, and alkoxy-group [-- desirable -- more than C [1-24], for example, a methoxy, -- Ethoxy ** butoxy, octyloxy, methoxyethoxy one, methoxy PENTA (ethyloxy), acryloyl oxyethoxy and pentafluoro propoxy] and an acyloxy machine (desirable -- more than C [1-24], for example, acetyloxy, --) benzoyloxy one and an alkoxy carbonyl group (desirable -- more than C [2-24], for example, a methoxycarbonyl, --) Ethoxycarbonyl, a cyano group, a fluoro machine, an alkoxy carbonyl group, a cyano group, and polymerization nature machines (preferably a vinyl group, an acryloyl machine, a methacryloyl machine, a styryl machine, a cinnamic acid residue, etc.) are mentioned. In the aforementioned general formula (I), n expresses three or more numbers.

[0036] The anion sections which constitute the salt of a <anion section> this invention are a sulfonamide, disulfon imide, N-acyl sulfonamide, alcohol, a phenol, and an anion which a proton comes to dissociate from at least one among sulfonic acids. As the aforementioned anion section, a sulfonamide, disulfon imide, and N-acyl sulfonamide are desirable.

[0037] As for the conjugate acid of the anion section, it is desirable that pKa is 11 or less, and it is more desirable that it is seven or less.

[0038] When the cation section which constitutes the salt of a <cation section> this invention is a metal ion belonging to a periodic table 1st (Ia) or the 2nd (IIa) group, unlike an oxy-alkylene machine, the atomic group shown by the general formula (I) does not interact with a cation strongly, but offers a flexible ionic conduction place from maneuverability being high. Thereby, the high ion transference number and high ion conductivity are realized.

[0039] As the cation section which constitutes the salt of this invention, the organic cation expressed with either the aforementioned general formula (II-a), the aforementioned general formula (II-b) and the aforementioned general formula (II-c) and/or a lithium ion are desirable.

[0040] In the aforementioned general formula (II-a), Qy1 expresses the atomic group which can form the aromatic cation of 5 member rings or 6 member rings with a nitrogen atom. Ry1 expresses the alkyl group or alkenyl machine which is not replaced [substitution or].

[0041] In the aforementioned general formula (II-b), Ay1 expresses a nitrogen atom or the Lynn atom. Ry1, Ry2, Ry3, and Ry4 express the alkyl group or alkenyl machine which is not replaced [substitution or]. Moreover, two or more of Ry1, Ry2, Ry3, and Ry4 may form the un-aromatic ring which connects mutually and contains Ay1.

[0042] In the aforementioned general formula (II-c), Ry1, Ry2, Ry3, Ry4, Ry5, and Ry6 may express the alkyl group or alkenyl machine which is not replaced [substitution or], among those two or more may connect them mutually, and they may form a ring structure.

[0043] The cation expressed with the aforementioned general formula (II-a), the aforementioned general formula (II-b), and the aforementioned general formula (II-c) may form a polymer through Qy1, or Ry1-Ry6.

[0044] In the aforementioned general formula (II-a), the composition atom of the atomic group Qy1 which can form the cation of aromatic series 5 or 6 member rings with nitrogen is preferably chosen from carbon, hydrogen, nitrogen, oxygen, and sulfur.

[0045] As 6 member rings completed by Qy1, it is a pyridine, a pyrimidine, a pyridazine, a pyrazine, and triazine, and is a pyridine more preferably.

[0046] As a aromatic-series 5 member ring completed by Qy1, it is an oxazole, a thiazole, an imidazole, a pyrazole, an isoxazole, thiadiazole, an OKISA diazole, and a triazole preferably, and they are an oxazole, a thiazole, and an imidazole more preferably. They are an oxazole and an imidazole especially preferably.

[0047] Setting to the aforementioned general formula (II-a), the aforementioned general formula (II-b), and the aforementioned general formula (II-c), Ry1-Ry6 are an alkyl group (even if carbon atomic numbers (henceforth, more than C) are 1-24 preferably and it is a straight chain-like, it may be branched-chain, and you may be a ring type.) which is not replaced [substitution or]. For example, the alkenyl machine which is not replaced [a methyl ethyl, a propyl, butyl, i-propyl, a pentyl, a hexyl, an octyl, 2-ethylhexyl, t-octyl, a desyl, a dodecyl, tetradecyl, 2-hexyl desyl, octadecyl, cyclohexyl, cyclopentyl, polymerization nature machines (preferably a vinyl group, an acryloyl machine, a methacryloyl machine, a styryl machine, a cinnamic acid residue, etc.), substitution, or] (you may be branched-chain, even if more than are 2- For example, a vinyl and an allyl compound are expressed, the alkyl group of more than C 3-18 or the alkenyl machine of more than C 2-18 is expressed preferably, and the alkyl group of more than C 4-6 is expressed more preferably.

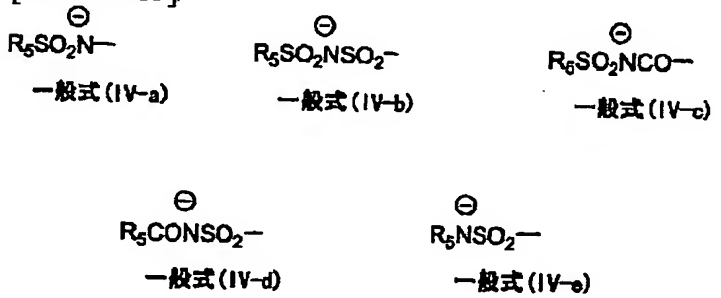
[0048] In the aforementioned general formula (II-a), the aforementioned general formula (II-b), and the aforementioned general formula (II-c), Qy1, and Ry1-Ry6 may have the substituent. As an example of a desirable substituent, a halogen atom (F, Cl, Br, I), A cyano group, an alkoxy group (a methoxy, ethoxy ** methoxyethoxy, etc.), aryloxy machines (phenoxy etc.) and an alkyl thio machine (a methylthio --) Acyl groups, such as an ethyl thio (an acetyl, a propionyl, benzoyl, etc.), a sulfonyl machine and an acyloxies (methane sulfonyl, benzenesulphonyl, etc.) machine (acetoxy --) Sulfonyloxy machine, such as benzoyloxy one (methane sulfo NIRIOKISHI) Phosphonyl groups, such as toluenesulfonyloxy (diethyl phosphonyl etc.), amide groups (acetylamino, benzoyl amide, etc.) and a carbamoyl group (N and N-dimethyl carbamoyl --) alkyl groups (a methyl, ethyl, and a propyl --), such as N-phenylcarbamoyl Aryl groups (a phenyl, toluyl, etc.), such as an isopropyl, a cyclo propyl, butyl, 2-carboxy ethyl, and a benzyl, heterocycle machines (for example, pyridyl, imidazolyl, furanyl, etc.), alkenyl machines (a vinyl, 1-propenyl, etc.), etc. are mentioned.

[0049] The polysiloxane salt expressed with the aforementioned general formula (III-a) or the aforementioned general formula (III-b) is desirable as a salt of a <salt structure> this invention.

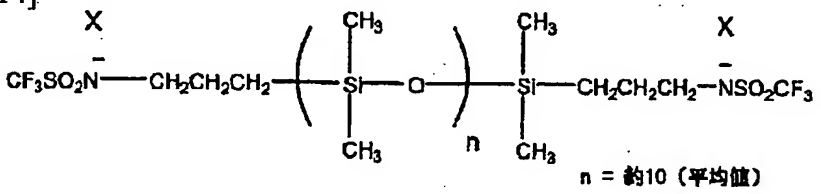
[0050] In the aforementioned general formula (III-a) and a general formula (III-b), R1 and R2 are the substituents and homonymy which were explained by the general formula (I). X1 and X2, and the cation section that ******(ed) are expressed, and even if these are the same, they may differ. L1 and L2 express the divalent connection machine containing the alkylene machine. Y1 and Y2 express the anion section mentioned above. Even if Y2 are the same as Y1, they may differ. R3 expresses the alkyl group which is not replaced [substitution or]. n expresses three or more numbers. In the aforementioned general formula (III-a) and the aforementioned general formula (III-b), the alkyl group which is not replaced [substitution or] is desirable as R1 and R2. As L1 and L2, a two or more-carbon number alkylene machine or an alkyleneoxy machine is desirable. As Y1 and Y2, the anion section expressed with a general formula (IV-e) from a general formula (IV-a) is desirable.

[0051]

[Formula 13]

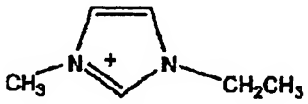


[0052] R5 in a general formula (IV-e) expresses the alkyl group which is not replaced [substitution or], an aryl group, or a heterocycle machine from a general formula (I-Va).
[0053] As the alkyl group, aryl group, and heterocycle machine of R5, what was explained in full detail by R1 of the aforementioned general formula (I) is used preferably. Especially, in the case of the aforementioned general formula (IV-a) to the aforementioned general formula (IV-c), a fluorine substitution alkyl group is desirable, and a trifluoromethyl machine and a pentafluoro ethyl group are still more desirable to it. In the case of the aforementioned general formula (IV-d), the fluorine substitution alkyl group and the substitution, or the non-replaced phenyl group of more than C 1-5 is desirable. In the case of the aforementioned general formula (IV-e), the phenyl group which is not replaced [substitution or] is desirable.
[0054] In the aforementioned general formula (III-a) and the aforementioned general formula (III-b), as for n, 3 to 30 is desirable, and 6 to 20 is more desirable.
[0055] Especially the desirable structure is as follows as a salt of this invention. Namely, it sets to the aforementioned general formula (III-a) or the aforementioned general formula (III-b). The above R1 and R2 is the alkyl groups of the carbon atomic numbers 1-3, and the above X1 and X2 is lithium ions. It is the divalent connection machine by which the above L1 and L2 is respectively expressed independently with either -(CH2) 3- and -(CH2) 3OCH2CH2-. Y1 and Y2 are the salts expressed with the structure which is a substituent containing the anion section respectively expressed with the structure of either the aforementioned general formula (IV-a) and the aforementioned general formula (IV-b) independently. In the aforementioned general formula (IV-a) and a general formula (IV-b), R5 expresses the alkyl group of the carbon atomic numbers 1-3.
[0056] Although the example of the salt which combined with below the anion structure of the salt used for the electrolyte constituent of this invention, cation structure, and them is shown, they cannot be combined arbitrarily and this invention is not necessarily limited to this.
[0057]
[Formula 14]



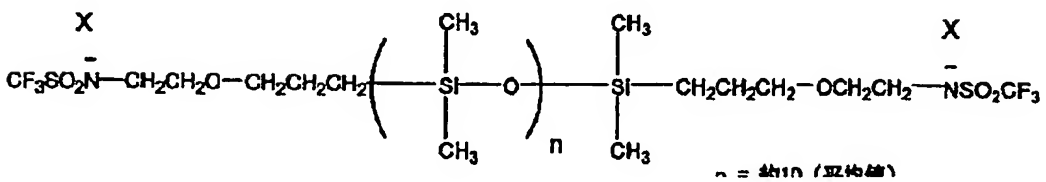
(P-1) X = Li^+

(P-2) X =

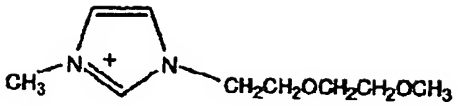


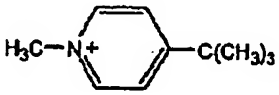
(P-3) X =

(P-4) X = $CH_3N(CH_2CH_3)_3^+$



(P-5) X = Li^+

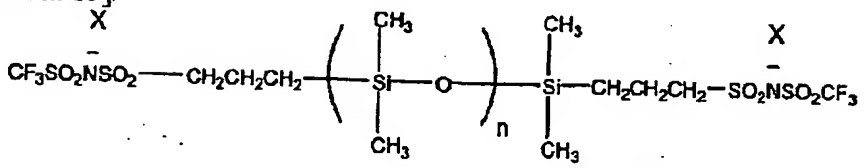
(P-6) X = 

(P-7) X = 

(P-8) X = $CH_3OCH_2CH_2\overset{+}{N}(CH_2CH_3)_3$

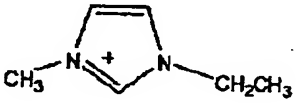
[0058]

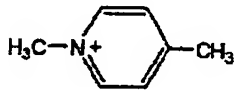
[Formula 15]



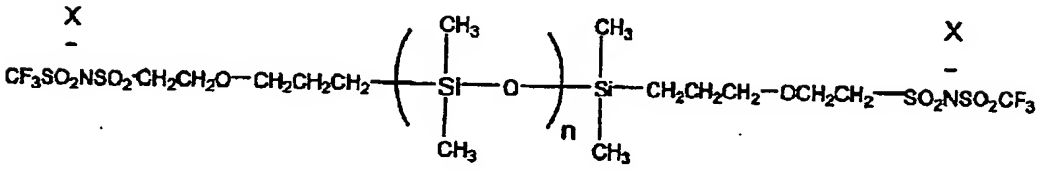
n=約10（平均値）

(P-9) X = Li^+

(P-10) X = 

(P-11) X = 

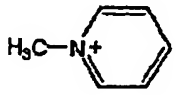
(P-12) X = $CH_3\overset{+}{N}(CH_2CH_3)_3$



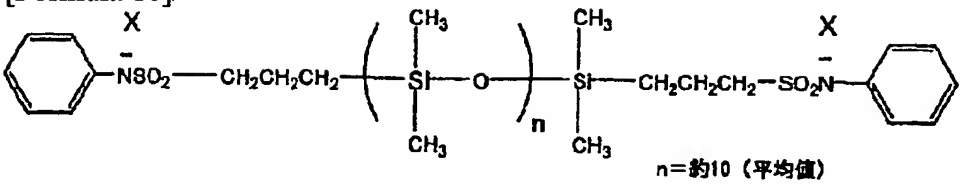
n=約30（平均値）

(P-13) X = Li^+

(P-14) X = 

(P-15) X = 

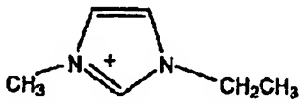
[0059]
[Formula 16]

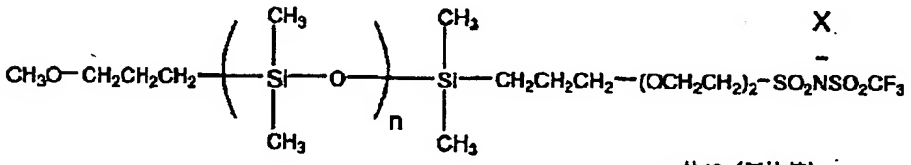


n=約10（平均値）

(P-16) X = Li^+

(P-17) X =

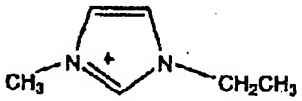


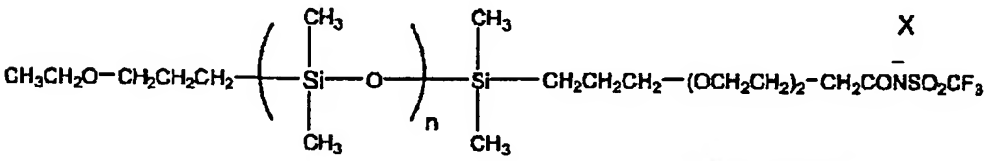


n=約10（平均値）

(P-18) X = Li^+

(P-19) X =

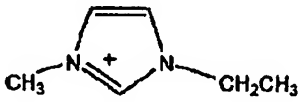




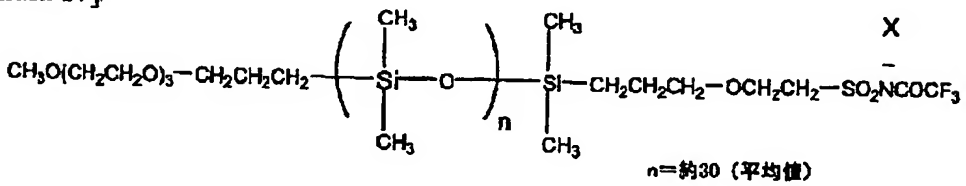
n=約30（平均値）

(P-20) X = Li^+

(P-21) X =



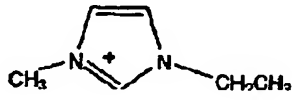
[0060]
[Formula 17]

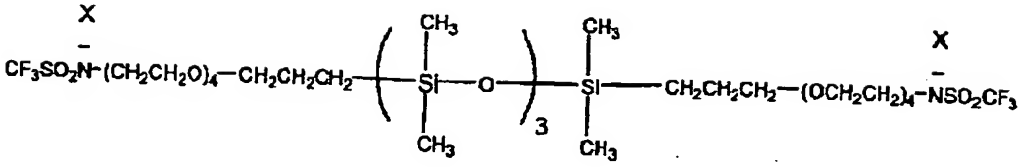


n=約30（平均値）

(P-22) X = Li^+

(P-23) X =

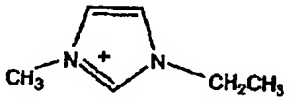




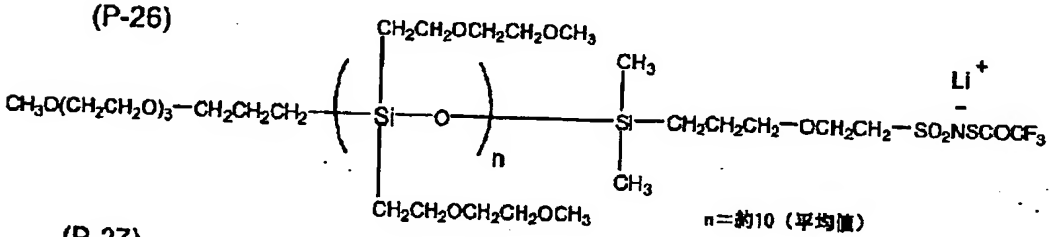
(P-24)

X = Li^+

(P-25)

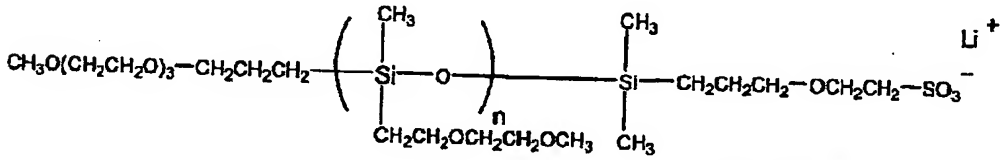
X = 

(P-26)



n=約10（平均値）

(P-27)

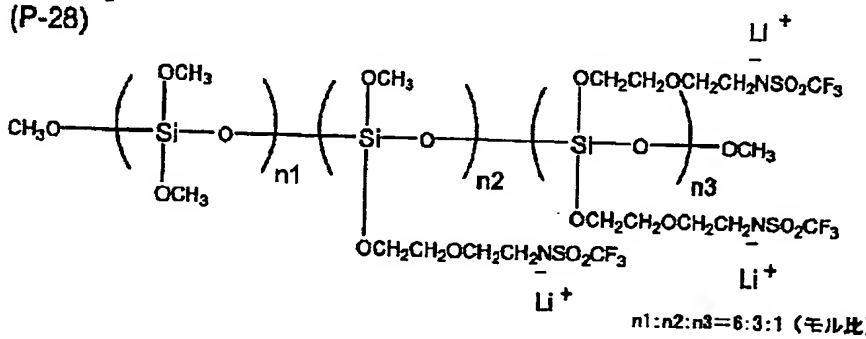


n=約10（平均値）

[0061]

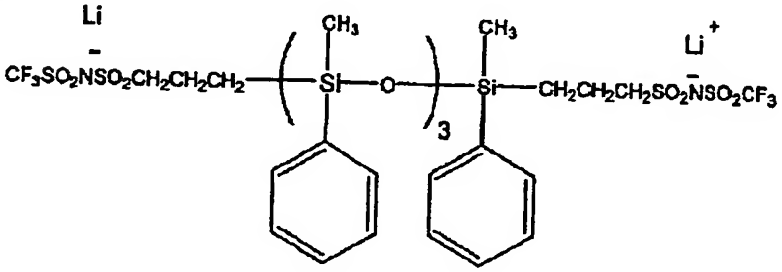
[Formula 18]

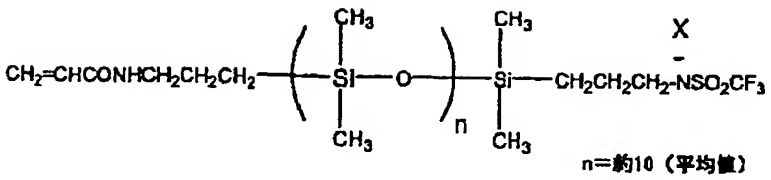
(P-28)



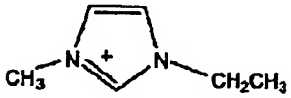
n1:n2:n3=6:3:1（モル比）

(P-29)

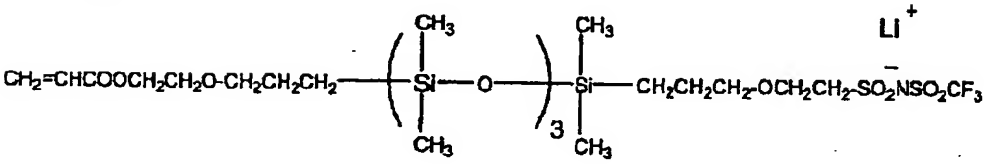




(P-30) X = Li^+

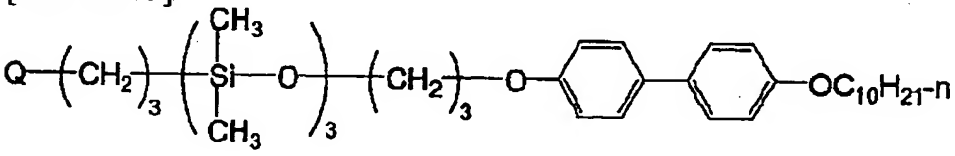
(P-31) X = 

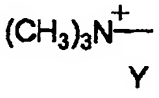
(P-32)



[0062]

[Formula 19]



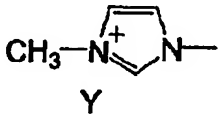
Q = 

(P-33) Y = I^-

(P-34) Y = $^-N(SO_2CF_3)_2$

(P-35) Y = BF_4^-

(P-36) Y = $CF_3SO_3^-$

Q = 

(P-37) Y = I^-

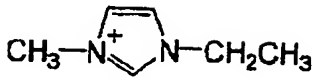
(P-38) Y = $^-N(SO_2CF_3)_2$

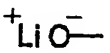
(P-39) Y = BF_4^-

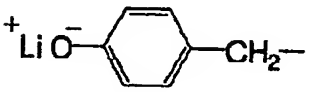
(P-40) Y = $CF_3SO_3^-$

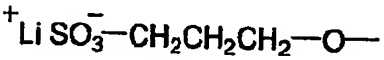
Q = $CF_3SO_2-N^-$ Y

(P-41) Y = Li^+

(P-42) Y = 

(P-43) Q = 

(P-44) Q = 

(P-45) Q = 

[0063] When using the electrolyte constituent of this invention for the electrolyte of a photoelectrochemical cell, it is desirable to use the electrolyte containing I- and I3- as a charge carrier, and it can add them in the form of arbitrary salts. As a desirable salt, YI- and YI3- mention, respectively and it is ****. Y is the cation section expressed with either the aforementioned general formula (II-a), the aforementioned general formula (II-b) and the aforementioned general formula (II-c) here. As for YI3-, it is common to add iodine (I2) to the bottom of YI-existence, and to make it generate in an electrolyte constituent. Added YI3- of I2 and the amount of said generates in that case.
[0064] Among the electrolyte constituent of this invention, the concentration of I- has desirable 10 - 90 mass %, and its 30 - 70 mass % is more desirable. It is desirable in that case that all the remaining components are the compounds of this invention expressed with a general formula (I).
[0065] It is more desirable that it is [0.1-20 mol] %, as for I3-, it is desirable that it is [0.1-50 mol / of I-] %, and it is / it is still more desirable that it is / 0.5-10 mol / %, and / most desirable that it is / 0.5-5 mol / %.
[0066] Still more nearly another fused salt may also be included in the electrolyte constituent of this invention. The fused salt used preferably combines the organic cation shown by the aforementioned general formula (II-a), the aforementioned general formula (II-b), and the aforementioned general formula (II-c), and arbitrary anions. As an anion, halogenide ion, SCN- (Cl-, Br-, etc.), BF4-, PF6-, ClO4-, 2 (CF3SO2)N-, 2 (CF3CF2SO2)N-, CH3SO3-, CF3SO3-, CF3COO-, Ph4B-, 3(CF3SO2) C-, etc. are mentioned as a desirable example, and it is more desirable that they are SCN-, CF3SO3-, CF3COO-, 2 (CF3SO2)N-, or BF4-. Moreover, alkali-metal salts, such as other iodine salts, such as LiI, CF3COOLi, CF3COONa, LiSCN, and NaSCN, can also be added. As for the addition of an alkali-metal salt, it is desirable that it is a 0.02 - 2 mass % grade, and its 0.1 - 1 mass % is still more desirable.
[0067] the electrolyte constituent of this invention -- LiI, NaI, KI, CsI, and CaI2 etc. -- a metal iodide -- The iodine salt of the 4th class imidazolium compound, the iodine salt of a tetraalkylammonium compound, Metal bromides, such as Br2, LiBr, NaBr, KBr, CsBr, and CaBr2, Or Br2 The bromine salt of the 4th class ammonium compounds, such as a tetrapod alkylammonium star's picture and a pyridinium star's picture Sulfur compounds, such as metal complexes, such as a ferrocyanic-acid salt-ferricyanic-acid salt and a ferrocene-ferricinium ion, the poly sodium sulfide, and alkyl thiol-alkyl disulfide, viologen coloring matter, a hydroquinone-quinone, etc. are made to contain, and can also be used. When making it contain, as for the amount of these compounds used, it is desirable that it is below 30 mass % of the whole electrolyte compound.
[0068] With the salt of this invention, a solvent can be preferably used to this compound and a

homogeneous amount at the maximum.
[0069] As for the solvent used for the electrolyte of this invention, it is desirable for a dielectric constant to be high in improving ionic mobility low, and for viscosity to be the compound which improves effective carrier concentration and can discover the outstanding ion conductivity. As such a solvent, carbonate compounds, such as ethylene carbonate and propylene carbonate, Heterocyclic compounds, such as 3-methyl-2-oxazolidinone, a dioxane, Ether compounds, such as diethylether, ethylene glycol dialkyl ether, The propylene-glycol dialkyl ether, the polyethylene-glycol dialkyl ether, Chain-like ether, such as the polypropylene-glycol dialkyl ether, A methanol, ethanol, ethylene glycol monoalkyl ether, Propylene-glycol monoalkyl ether, polyethylene-glycol monoalkyl ether, Alcohols, such as polypropylene-glycol monoalkyl ether, Ethylene glycol, a propylene glycol, a polyethylene glycol, Polyhydric alcohol, such as a polypropylene glycol and a glycerol, an acetonitrile, Guru taro dinitrile, a methoxy acetonitrile, a propionitrile, Non-proton polar substances, such as ester, such as nitryl compounds, such as a benzonitrile, a carboxylate, phosphoric ester, and phosphonate, a dimethyl sulfoxide, and a sulfolane, water, etc. can be used. Also in this, nitryl compounds, such as heterocyclic compounds, such as carbonate compounds, such as ethylene carbonate and propylene carbonate, and 3-methyl-2-oxazolidinone, an acetonitrile, guru taro dinitrile, a methoxy acetonitrile, a propionitrile, and a benzonitrile, and especially ester are desirable. Even if it uses these independently, they may use two or more sorts together.
[0070] As a solvent, from a viewpoint of the improvement in endurance by volatility-proof, a thing 200 degrees C or more has the desirable boiling point in an ordinary pressure (one atmospheric pressure), a thing 250 degrees C or more is more desirable, and a thing 270 degrees C or more is still more desirable.
[0071] When using the electrolyte constituent of this invention for electrochemical cells, such as a lithium ion battery, it considers as the electrolyte constituent which added lithium salt. In this case, the anion of the lithium salt used An imido anion (CF3 SO2) (2 N-, 2 (CF3 CF2 SO2)N-) or boron (B), It is more desirable that they are the fluoride anions (BF4-, PF6-, CF3 SO3-, C(CF3SO2)3-, etc.) containing at least one or more kinds of elements chosen from Lynn (P) and sulfur (S). As concentration of the salt at that time, 1 mass % to 70 mass % is desirable to the compound of a general formula (I), and 20 mass % to 50 mass % is still more desirable.
[0072] (Electrochemical cell) The electrochemical cell of this invention is characterized for the aforementioned electrolyte constituent of this invention by ******. As a mode of the electrochemical cell of this invention, a photoelectrochemical cell and a non-water rechargeable battery are mentioned.
[0073] The photoelectrochemical cell by which the electrolyte of this invention is preferably used below for a <photoelectrochemical cell> is explained. It enables it to use the photoelectrochemical cell of this invention for the cell use which makes an optoelectric transducer work in an external circuit, and it has the photosensitive layer and charge transfer layer containing the semiconductor which induces a radiant ray, and a counter electrode. The electrolyte constituent of this invention contains in this charge transfer layer.
[0074] The photoelectrochemical cell of this invention which used the electrolyte constituent of this invention for below is explained. The photoelectrochemical cell of this invention has the charge transporting bed containing the aforementioned electrolyte constituent, a photosensitive layer containing the semiconductor by which sensitization was carried out with coloring matter, and a counter electrode, and it constitutes them so that the optoelectric transducer explained to the so-called following may be made to work in an external circuit. The photoelectrochemical cell of this invention shows the outstanding endurance with small degradation of the cell performance in the passage of time while it is excellent in a photo-electric-translation performance, since the aforementioned charge transporting bed contains the electrolyte constituent of this invention.
[0075] - An example of an optoelectric transducer applicable to this invention at optoelectric-transducer- drawing 1 is shown. An optoelectric transducer 10 comes to carry out the laminating of a

conductive layer 12, an under coat 14, a photosensitive layer 16, the charge transporting bed 18, and the counter electrode conductive layer 20 one by one. A photosensitive layer 16 turns into the semiconductor layer 24 which carried out sensitization with coloring matter d from the charge transportation material t. The semiconductor layer 24 is a porous layer which consists of a semiconductor particle s, the opening was formed between the semiconductor particles s and the charge transportation material t has permeated this opening. The charge transportation material t consists of the same component as the material used for the charge transporting bed 18. Under the conductive layer 12, the substrate 28 is arranged under the substrate 26 and the counter electrode conductive layer 20. Substrates 26 and 28 may be for giving intensity, and may not be in an optoelectric transducer. Moreover, on the boundary of each layer, for example, the boundary of a conductive layer 12 and a photosensitive layer 16, the boundary of a photosensitive layer 16 and the charge transporting bed 18, and the boundary of the charge transporting bed 18 and the counter electrode conductive layer 20, the constituents of each class may be carrying out diffusive mixing mutually. In addition, a conductive layer 12, a substrate 26, and/or the counter electrode conductive layer 20 and substrate 28 of the side which may carry out incidence of the light to an optoelectric transducer 10 from either or both sides, and carries out incidence of the light to it can consist of material which has light-transmission nature, respectively.

[0076] Next, an operation of an optoelectric transducer 10 is explained. In addition, the case where the semiconductor particle s is n type is explained. If light carries out incidence to an optoelectric transducer 10, the light which carried out incidence will reach a photosensitive layer 16, will be absorbed with coloring matter d etc., and will generate the coloring matter d of an excitation state. The excited coloring matter d passes the electron of a high energy to the conduction band of the semiconductor particle s, and it becomes an oxidant itself. The electron from which it moved to the aforementioned conduction band reaches a conductive layer 12 by the network of the semiconductor particle s. Therefore, a conductive layer 12 has an electronegative potential to the counter electrode conductive layer 20. In the mode which used the optoelectric transducer 10 for the photoelectric cell, if this photoelectric cell is connected with an external circuit, the electron in a conductive layer 12 will reach the counter electrode conductive layer 20, working in an external circuit. The generated reductant (for example, I3-) returns the oxidant of coloring matter d, and returns an electron while it returns this electrolyte component (for example, I-), when charge transportation material is an electrolyte. By continuing irradiating light, a series of reactions occur succeedingly and can take out the electrical and electric equipment.

[0077] Hereafter, an usable material and its formation method are explained to each class of the aforementioned optoelectric transducer. In addition, when calling it "a conductive base material" below, it is accepted conductive-layer 12, and although it consists of a conductive layer 12 and a substrate 26 which it is arbitrary and is prepared, when calling it a "counter electrode" including both sides, it is accepted counter electrode conductive-layer 20, and both sides are included although it consists of a counter electrode conductive layer 20 and a substrate 26 which it is arbitrary and is prepared.

[0078] (A) A conductive base material conductivity base material consists of the monolayer of (1) conductive layer or (2) conductive layers, and two-layer [of a substrate]. In the case of (1), material at which intensity and sealing performance are fully maintained as a conductive layer is used. For example, a metallic material (alloys containing these, such as platinum, gold, silver, copper, zinc, titanium, and aluminum) can be used. In the case of (2), the substrate which has the conductive layer which contains an electric conduction agent in a photosensitive-layer side can be used. As a desirable electric conduction agent, a metal (for example, alloys containing these, such as platinum, gold, silver, copper, zinc, titanium, aluminum, and an indium), carbon, or conductive metallic oxides (what doped a fluorine or antimony to an indium-tin multiple oxide and the tin oxide) are mentioned. The thickness of a conductive layer has desirable about 0.02-10 micrometers.

[0079] A conductive base material has surface electrical resistance as good as a low. Below 50ohms /

** of the range of surface electrical resistance are desirable, and it is more desirable. [of below 20ohms / **]

[0080] When irradiating light from a conductive base material side, as for a conductive base material, it is desirable that it is substantially transparent. It means substantially that permeability is it 10% or more that it is transparent in some or the whole region of light of a visible - near infrared region (400-1200nm), it is desirable that it is 50% or more, and 80% or more is more desirable. It is desirable that the permeability of the wavelength region where a photosensitive layer has sensitivity especially is high.

[0081] What formed the transparent conductive layer which consists of a conductive metallic oxide in the front face of transparent substrates, such as glass or plastics, by an application or vacuum evaporationo as a transparent conductivity base material is desirable. As a transparent conductive layer, the diacid-ized tin or indium-stannic-acid ghost (ITO) which doped a fluorine or antimony is desirable. A transparent polymer film besides glass substrates, such as an advantageous soda glass and an alkali free glass without the influence of alkali elution, can be used for a transparent substrate in respect of a low cost and intensity. As a material of a transparent polymer film, there is a triacetyl-cellulose (TAC), polyethylene-terephthalate (PET), polyethylenenaphthalate (PEN), syndiotactic polystyrene (SPS), polyphenylene-sulfide (PPS), polycarbonate (PC), polyarylate (PAr), polysulfone (PSF), polyester sulfone (PES), polyimide (PI), polyether imide (PEI), annular polyolefine, and bromine-ized phenoxy etc. In order to secure sufficient transparency, as for the coverage of a conductive metallic oxide, it is desirable to consider as per [0.01-100g] two 1m of base materials of glass or plastics.

[0082] It is desirable to use a metal lead in order to lower resistance of a transparent conductivity base material. The quality of the material of a metal lead has desirable metals, such as platinum, gold, nickel, titanium, aluminum, copper, and silver. As for a metal lead, it is desirable to prepare the transparent conductive layer which installs in a transparent substrate by vacuum evaporationo, sputtering, etc., and becomes it from conductive tin oxide or a conductive ITO film on it. The fall of the amount of incident lights by metal lead installation may be 1 - 5% more preferably less than 10%.

[0083] (B) The photosensitive-layer aforementioned photosensitive layer absorbs light, performs charge separation, and has the function which produces an electron and an electron hole. The aforementioned photosensitive layer contains the semiconductor by which coloring matter sensitization was carried out. With the semiconductor by which coloring matter sensitization was carried out, generating of an optical absorption, the electron by this, and an electron hole takes place mainly in coloring matter, and a semiconductor bears the role which receives and transmits this electron (or electron hole). As for the semiconductor used by this invention, it is desirable that it is the n-type semiconductor which gives an anode current by a conductor electron serving as a carrier under optical pumping.

[0084] (B-1) The compounds (for example, a strontium titanate, titanic-acid calcium, titanic-acid sodium, a barium titanate, a niobic-acid potassium, etc.) which have silicon, an element semiconductor like germanium, a III-V system compound semiconductor, metaled chalcogenide (for example, an oxide, a sulfide, selenides, or those composites etc.), or a perovskite structure as a semiconductor semiconductor can be used.

[0085] As chalcogenide of a desirable metal, the oxide of titanium, tin, zinc, iron, a tungsten, a zirconium, a hafnium, strontium, an indium, a cerium, an yttrium, a lanthanum, vanadium, niobium, or a tantalum, cadmium, zinc, lead, silver, antimony or the sulfide of a bismuth, cadmium or a leaden selenide, the telluride of cadmium, etc. are mentioned. As other compound semiconductors, the selenide of phosphides, such as zinc, a gallium, an indium, and cadmium, a gallium arsenide, or a copper-indium, the sulfide of a copper-indium, etc. are mentioned. Furthermore, the composite expressed with MxOySz or M1xM2yOz (the number [metallic element] of combination with which an oxygen atom, x, and y and z become as for M, M1, and M2, and, as for O, a valence becomes neutral, respectively) can also be used preferably.

[0086] As an example of the semiconductor used for this invention, Si, TiO2, SnO2, Fe 2O3, WO3, ZnO, Nb 2O5, CdS, ZnS and PbS, Bi2S3, CdSe, CdTe, SrTiO3, GaP, InP, GaAs, CuInS2, and CuInSe2 grade are desirable. TiO2, ZnO, SnO2, Fe 2O3, WO3 and Nb 2O5, CdS and PbS, CdSe, SrTiO3 and InP, GaAs, CuInS2, or CuInSe2 is more desirable, TiO2 or especially Nb 2O5 is desirable, and TiO2 is the most desirable. TiO2 has desirable TiO2 which includes an anatase type crystal 70% or more, and especially TiO2 of 100% anatase type crystal is desirable. Moreover, it is also effective to dope a metal in order to raise the electronic conductivity in these semiconductors. As a metal to dope, divalent and a trivalent metal are desirable. It is the purpose which prevents that a reverse current flows from a semiconductor to a charge transporting bed, and it is also effective to dope a univalent metal to a semiconductor.
[0087] Although a single crystal or a polycrystal is sufficient as the semiconductor used for this invention, viewpoints, such as a manufacturing cost, raw-material reservation, and an energy pay back time, to its polycrystal is desirable, and especially its porous membrane that consists of a semiconductor particle is desirable. Moreover, the amorphous portion may be included in part.
[0088] Generally the particle size of a semiconductor particle is the order of nm-mu m. As for the mean particle diameter of the primary particle which asked for projected area from the diameter when converting into a circle, it is desirable that it is 5-200nm, and its 8-100nm is more desirable. Moreover, the mean particle diameter of the semiconductor particle in dispersion liquid (aggregated particle) has desirable 0.01-30 micrometers. It is 10nm or less preferably [may mix two or more kinds of particles from which a particle size distribution differs, and / that the average size of a small particle is 25nm or less in this case], and more preferably. Particle size is big, for example, it is also desirable to mix a semiconductor particle (100nm or more and about 300nm) in order to scatter an incident light and to raise the rate of optical capture.
[0089] The number of the kinds of semiconductor particle one, and they may be two or more sorts of different mixtures. When mixing and using two or more sorts of semiconductor particles, as for one sort, it is desirable that they are TiO2, ZnO, Nb 2O5, or SrTiO3. Moreover, as one more sort, it is desirable that they are SnO2, Fe2O3, and WO3. As a still more desirable combination, combination, such as ZnO, SnO2, ZnO and WO3, or ZnO, SnO2, WO3, can be mentioned. When mixing and using two or more sorts of semiconductor particles, each particle size may differ. The particle size of the semiconductor particle especially mentioned at the one above-mentioned item is large, and combination with the small semiconductor particle mentioned henceforth [2 items] is desirable. The particle of a desirable large particle size is 100nm or more, and the particle of a small particle size is 15nm or less in combination.
[0090] a sol-gel method given [as a method of producing a semiconductor particle] in "the thin-layer-coating technology by the sol-gel method" (1995) etc. of the company (1998) of the "science of sol-gel method" AGUNE ** style of ********, and a technical-information association, and "composition of the monodisperse particle by the new synthesis method gel-sol method and size form control" of Tadao Sugimoto -- wait -- ****, the 35th volume, No. 9, and the gel-sol method of a 1012-1018 pages (1996) publication Moreover, the method of producing an oxide for the chloride which Degussa developed by elevated-temperature hydrolysis in an acid hydrogen salt is also desirable.
[0091] Although both the above-mentioned sol-gel method the gel-sol method and the elevated-temperature adding-water part solution method in the inside of the acid hydrogen salt of a chloride are desirable when a semiconductor particle is titanium oxide, the sulfuric-acid method and chlorine method of a publication can also be further used for "titanium oxide physical-properties and applied-technology" Gihodo Shuppan Co., Ltd. (1997) of the Seino study. Furthermore, the method of Barbe's and others journal OBU American ceramic society, the 80th volume, No. 12, and a 3157-3171 pages (1997) publication and the method of Burnside's and others chemistry OBU MATERIARUZU, the 10th volume, No. 9, and a 2419-2425-page publication are also desirable as a sol-gel method.
[0092] (B-2) The semiconductor particle layer aforementioned semiconductor is used with the form

of the semiconductor particle layer formed for example, on the aforementioned conductive base material. In order to apply a semiconductor particle on a conductive base material, the above-mentioned sol-gel method etc. can also be used besides the method of applying the dispersion liquid or the colloidal solution of a semiconductor particle on a conductive base material. When mass-production-izing of an optoelectric transducer, the physical properties of semiconductor particle liquid, the versatility of a conductive base material, etc. are taken into consideration, the wet film production method is comparatively advantageous. As the wet film production method, the applying method, print processes, an electrolytic-deposition method, and an electrodeposition process are typical. Moreover, the SPD method which sprays the metallic-oxide precursor pyrolyzed on the method of carrying out vacuum evaporationo by the method (the LPD method) of depositing by the liquid phase by the ligand exchange etc., the spatter, etc., CVD, or the warmed substrate from the method of oxidizing a metal and a metal solution, and forms a metallic oxide can also be used.

[0093] In case the method of distributing while grinding using the method and mill which are mashed with the mortar other than the above-mentioned sol-gel method as a method of producing the dispersion liquid of a semiconductor particle, or a semiconductor is compounded, the method of depositing as a particle and using it as it is in a solvent, etc. is mentioned.

[0094] As a dispersion medium, water or various kinds of organic solvents (for example, a methanol, ethanol, isopropyl alcohol, a citronellol, terpineol, a dichloromethane, an acetone, an acetonitrile, ethyl acetate, etc.) are mentioned. You may use polymer like a polyethylene glycol, a hydroxyethyl cellulose, and a carboxymethyl cellulose, a surfactant, an acid, or a chelating agent as a distributed assistant if needed in the case of distribution. Since the semiconductor layer which regulation of the viscosity of dispersion liquid is attained and cannot separate further easily due to changing the molecular weight of a polyethylene glycol can be formed or the voidage of a semiconductor layer can be controlled, it is desirable to add a polyethylene glycol.

[0095] As the method of application, a roller, the dipping method of the air knife method and the blade method, etc. are desirable as a metering system as an application system. Moreover, the slide hopper method given in application, the wire bar method currently indicated by JP,58-4589,B as that by which metering is made into the same portion, U.S. JP,2681294,B, said 2761419 numbers, said 2761791 numbers, etc., the extrusion method, the curtain method, etc. are desirable. Moreover, the spin method and a spray method are also desirable as a general aviation. As the wet printing method, letterpress, offset, and the three major print processes of gravure are begun, and intaglio printing, the rubber version, screen-stencil, etc. are desirable. According to liquid viscosity or wet thickness, the desirable film production method is chosen from these.

[0096] The layer of a semiconductor particle can carry out the multilayer application of the dispersion liquid of the semiconductor particle from which not only a monolayer but particle size is different, or can also carry out the multilayer application of the application layer containing the semiconductor particle (or a different binder, a different additive) from which a kind differs. When thickness is insufficient, the multilayer application is effective at a one-time application.

[0097] Since the amount of support coloring matter per unit projected area generally increases so that semiconductor particle layer thickness (it is the same as the thickness of a photosensitive layer) becomes thick, although the rate of capture of light becomes high, since the generated diffusion length of electron increases, the loss by charge reunion also becomes large. Therefore, the thickness with a desirable semiconductor particle layer is 0.1-100 micrometers. When using for a photoelectric cell, semiconductor particle layer thickness has desirable 1-30 micrometers, and its 2-25 micrometers are more desirable. The coverage which receives per two 1m of base materials of a semiconductor particle has 0.5-desirable 100g, and 3-its 50g are more desirable.

[0098] Heat-treating is desirable, in order to raise improvement in paint film intensity, and adhesion with a base material, while contacting semiconductor particles electronically, after applying a semiconductor particle on a conductive base material. The range of heating temperature has 40 degrees C or more desirable 700 degrees C or less, and is more desirable. [of 100 degrees C or more

600 degrees C or less] Moreover, heating time is 10 minutes - about 10 hours. When using the low base material of the melting point or softening temperature like a polymer film, high temperature processing is not desirable in order to cause degradation of a base material. Moreover, it is desirable that it is low temperature (for example, 50 degrees C - 350 degrees C) as much as possible also from the viewpoint of cost. Low temperature-ization can also be performed by becoming possible by the small semiconductor particle 5nm or less, heat-treatment under existence of a mineral acid and a metallic-oxide precursor, etc., and impressing irradiation of ultraviolet rays, infrared radiation, microwave, etc., electric field, and an ultrasonic wave. It is desirable to use together for the purpose which removes the unnecessary organic substance etc. simultaneously, combining suitably heating besides the above-mentioned irradiation or impression, reduced pressure, oxygen plasma treatment, pure water washing, solvent cleaning, gas scrubbing, etc.

[0099] It is the purpose which the surface area of a semiconductor particle is increased, or raises the purity near the semiconductor particle after heat-treatment, and raises the electron-injection efficiency from coloring matter to a semiconductor particle, for example, chemical-plating processing using titanium-tetrachloride solution and electrochemical plating processing using titanium-trichloride solution may be performed. Moreover, it is the purpose which prevents that a reverse current flows from a semiconductor particle to a charge transporting bed, and it is effective to also make the low organic substance of electronic conductivity other than coloring matter stick to a particle front face. The object which has a hydrophobic radical as the organic substance made to adsorb is desirable.

[0100] As for a semiconductor particle layer, it is desirable to have a big surface area so that much coloring matter can be adsorbed. As for the surface area in the state where the layer of a semiconductor particle was applied on the base material, it is desirable that they are 10 or more times to projected area, and it is more desirable that they are 100 or more times. Although especially a limit does not have this upper limit, they are usually about 1000 times.

[0101] (B-3) If it is the compound which can carry out sensitization of the semiconductor, the sensitizing dye used for a coloring matter photosensitive layer has absorption in a visible region or a near-infrared region, and can use it for arbitration, and organometallic complex coloring matter, methine coloring matter, porphyrin system coloring matter, or its phthalocyanine system coloring matter is desirable. Moreover, since the wavelength region of photo electric translation is made large as much as possible and a conversion efficiency is gathered, two or more kinds of coloring matter can be used together or mixed. In this case, the coloring matter used together or mixed and its rate can be chosen so that it may double with the target wavelength region and intensity distribution of the light source.

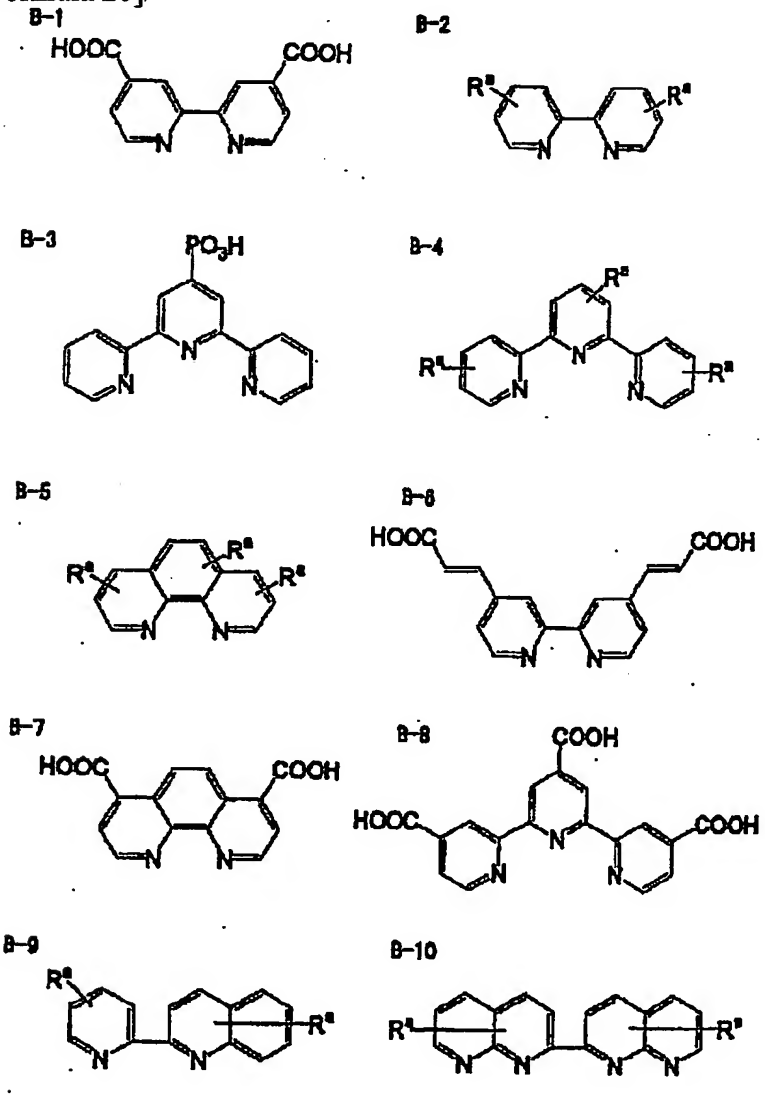
[0102] It is desirable to have the suitable joint machine (interlocking group) which has the adsorption capacity force to the front face of a semiconductor particle as coloring matter. The chelation machine which has pi conductivity like a COOH basis, OH basis, SO3H set, -P(O) (OH)2 set, an acidic group like -OP(O) (OH)2 set or an oxime, dioxime, a hydroxyquinoline, salicylate, or alpha-KETOENO rate as a desirable joint machine is mentioned. Especially, a COOH basis, -P(O) (OH)2 set, or especially -OP(O) (OH)2 set is desirable. These bases may form alkali metal etc. and the salt, and may form the inner salt. Moreover, when it contains an acidic group like [in case a methine chain forms a squarylium ring and a crocodile NIUMU ring] in the case of poly methine coloring matter, you may have this portion as a joint machine.

[0103] Hereafter, the desirable sensitizing dye used for a photosensitive layer is explained concretely.

(B-3-a) When organometallic complex coloring matter coloring matter is metal complex coloring matter, metal phthalocyanine dye, metalloporphyrin coloring matter, or ruthenium complex coloring matter is desirable, and especially ruthenium complex coloring matter is desirable. as ruthenium complex coloring matter -- for example, U.S. JP,4927721,B -- said -- No. 4684537 -- said -- No. 5084365 -- said -- No. 5350644 -- said -- No. 5463057 -- said -- the complex coloring matter of a publication is mentioned to each official report, such as each specification, such as No. 5525440, and

JP,7-249790,A, ****** No. 504512 [ten to], the world patent 98/No. 50393, and JP,2000-26487,A
[0104] Furthermore, when the aforementioned coloring matter is ruthenium complex coloring matter, the ruthenium complex coloring matter expressed with the following general formula (V) is desirable.

[0105] General formula (V)
(A1) In the tRu(B-a) u(B-b) v(B-c) w aforementioned general formula (V), A1 expresses the ligand of 1 or 2 seats. As for A1, it is desirable that it is the ligand chosen from the group which consists of a derivative of Cl, SCN, H2O, Br, I, CN and NCO, SeCN, beta-diketones, oxalic acid, and a dithiocarbamic acid. When t is two or more, even if two or more A1 is the same, it may differ. B-a, B-b, and B-c express independently the ligand expressed with the following formula (B-1) - (B-10) either among the aforementioned general formula (V), respectively. t expresses the integer of either 0-3, and u, v, and w are together put suitably according to the kind of ligand so that the ruthenium complex which expresses 0 or 1 respectively and is expressed with the aforementioned general formula (V) may turn into six coordinated complexes.
[0106]
[Formula 20]



[0107] Among aforementioned formula (B-1) - (B-10), Ra expresses a hydrogen atom or a substituent and the aryl group which is not replaced [the substitution of the aralkyl machine which is not replaced / the substitution of the alkyl group which is not replaced / the substitution of a halogen

atom and the carbon atomic numbers 1-12 or / and the carbon atomic numbers 7-12 or / and the carbon atomic numbers 6-12 or], an acidic group (these acidic groups may form the salt), or a chelation machine is mentioned as The shape of a straight chain and the letter of branching are sufficient as the alkyl portions of an alkyl group and an aralkyl machine. Moreover, a monocycle or a polycyclic (the condensed ring, ring set) is sufficient as the aryl portions of the aforementioned aryl group and an aralkyl machine. Among the aforementioned general formula (V), even if B-a, B-b, and B-c are the same, they may differ.

[0108] Although the desirable example (instantiation compound R-1 to R-17) of organometallic complex coloring matter is shown below, the coloring matter used for this invention is not limited to the following examples.

[0109]

[Formula 21]

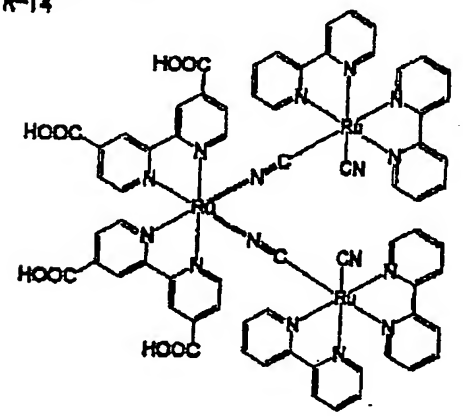
$(A^1)_pRu(B-a)(B-b)(B-c)$

	A^1	p	B-a	B-b	B-c	R^a
R-1	SCN	2	B-1	B-1	—	—
R-2	CN	2	B-1	B-1	—	—
R-3	Cl	2	B-1	B-1	—	—
R-4	CN	2	B-7	B-7	—	—
R-5	SCN	2	B-7	B-7	—	—
R-6	SCN	2	B-1	B-2	—	H
R-7	SCN	1	B-1	B-3	—	—
R-8	Cl	1	B-1	B-4	—	H
R-9	I	2	B-1	B-5	—	H
R-10	SCN	3	B-8	—	—	—
R-11	CN	3	B-8	—	—	—
R-12	SCN	1	B-2	B-8	—	H
R-13	—	0	B-1	B-1	B-1	—

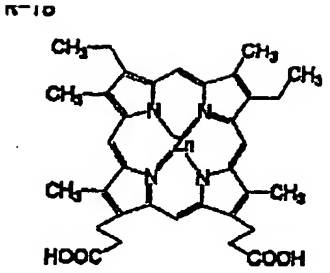
[0110]

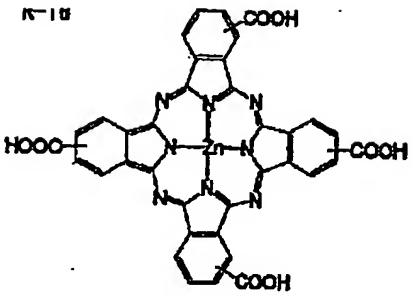
[Formula 22]

R-14

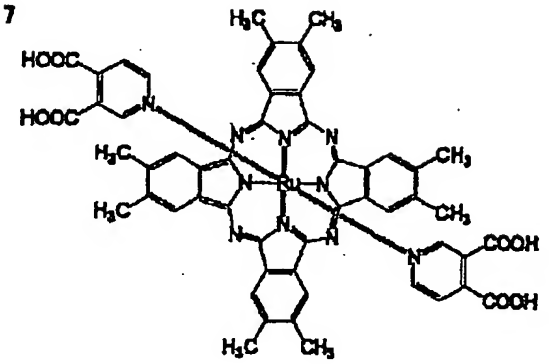


R-15





R-17

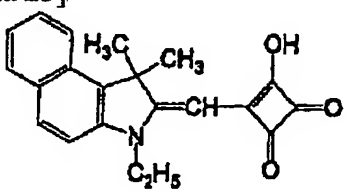


[0111] (B-3-b) The desirable methine coloring matter used for a methine coloring matter this invention is poly methine coloring matter, such as a cyanine dye, merocyanine coloring matter, and SUKUWARIRIUMU coloring matter. As poly methine coloring matter preferably used by this invention, the coloring matter of a publication is mentioned in each specification of each official report of JP,11-35836,A, JP,11-67285,A, JP,11-86916,A, JP,11-97725,A, JP,11-158395,A, JP,11-163378,A, JP,11-214730,A, JP,11-214731,A, JP,11-238905,A, and JP,2000-26487,A, the Europe patent No. 892411, said 911841 numbers, and said 991092 numbers, for example. The example of desirable methine coloring matter is shown below.

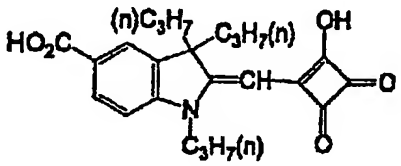
[0112]

[Formula 23]

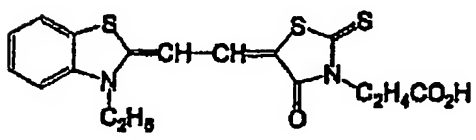
M-1



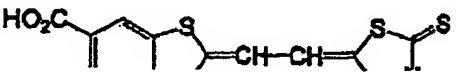
M-2

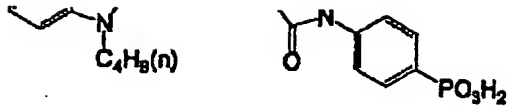


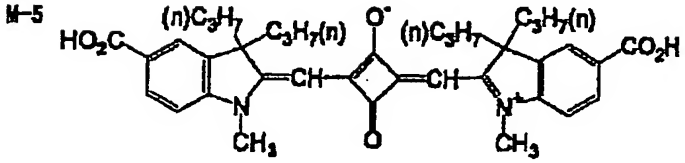
M-3



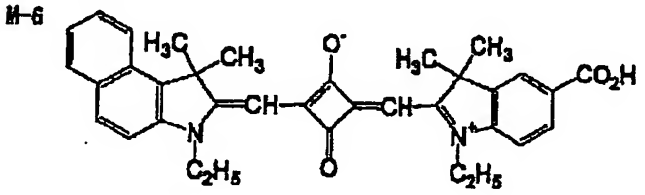
M-4

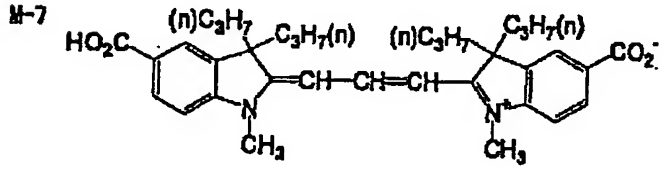


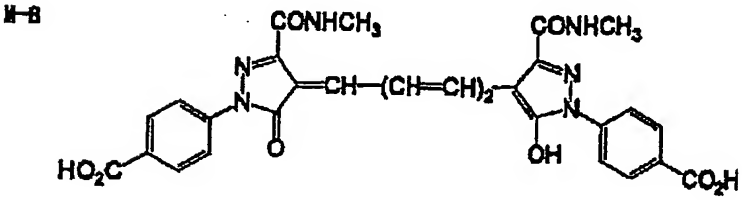




[0113]
[Formula 24]







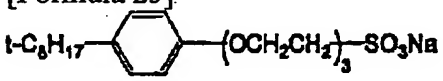
[0114] (B-4) In order to make coloring matter stick to the adsorption semiconductor particle of the coloring matter to a semiconductor particle, the method which is immersed in the conductive base material which has the semiconductor particle layer dried well in the solution of coloring matter, or applies the solution of coloring matter to a semiconductor particle layer can be used. In the case of the former, dip coating, the dipping method, a roller, the air knife method, etc. are usable. In the case of dip coating, adsorption of coloring matter may be performed at a room temperature, and you may perform it by carrying out heating reflux as indicated by JP,7-249790,A. Moreover, as the latter method of application, there are the wire bar method, the slide hopper method, the extrusion method, the curtain method, the spin method, a spray method, etc. one desirable as a solvent which dissolves coloring matter -- for example, alcohols (a methanol --) nitril (an acetonitrile --), such as ethanol, t-butanol, and benzyl alcohol Nitromethanes, such as a propionitrile and 3-methoxy propionitrile, a halogenated hydrocarbon (a dichloromethane, a dichloroethane, and chloroform --) Ether, such as a chlorobenzene (diethylether, tetrahydrofuran, etc.), dimethyl sulfoxide and amides (N.N-dimethylformamide --) N-methyl pyrrolidones, such as N and N-dimethyl acetamido, 1, 3-dimethyl imidazolidinone, 3-methyl oxazolidinone and ester (ethyl acetate, butyl acetate, etc.) Carbonates (diethyl carbonate, an ethylene carbonate, propylene carbonate, etc.), ketones, hydrocarbons (an acetone, 2-butanone, cyclohexanone, etc.) (Korean geisha, the petroleum ether, benzene, toluene, etc.), and these mixed solvents are mentioned.

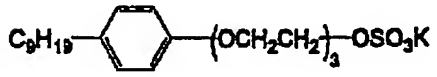
[0115] All the amounts of adsorption of coloring matter have desirable per [a unit surface area

(1m2) / 0.01] - 100mmol of a porosity semiconductor-electrode substrate. Moreover, as for the amount of adsorption to the semiconductor particle of coloring matter, it is desirable that it is the range per [0.01] 1g of semiconductor particles - of 1mmol. By considering as the coloring matter amount of adsorption of the aforementioned range, the sensitization effect in a semiconductor is fully acquired. On the other hand, if there is too little coloring matter, the sensitization effect will become inadequate, and if there is too much coloring matter, the coloring matter which has not adhered to a semiconductor will float, and it becomes the cause of reducing the sensitization effect. In order to increase the amount of adsorption of coloring matter, heat-treating before adsorption is desirable. After heat-treatment, in order to avoid that water sticks to a semiconductor particle front face, it is desirable to perform adsorption operation of coloring matter quickly [while the temperature of a semiconductor-electrode substrate is 60-150 degrees C], without returning to ordinary temperature. Moreover, for the purpose which reduces interactions, such as condensation between coloring matter, a colorless compound may be added to coloring matter and a coadsorption may be carried out to a semiconductor particle. The sulfonates like a steroid compound (for example, chenodeoxycholic acid) or the following example which the effective compound for this purpose is a compound with a surface activity property and structure, for example, have a carboxyl group are mentioned.

[0116]

[Formula 25]





[0117] As for non-adsorbed coloring matter, it is desirable that washing removes promptly after adsorption. It is desirable to use a wet washing tub and to wash by organic solvent like polar solvents, such as an acetonitrile, and an alcohols solvent. After adsorbing coloring matter, amines and the 4th class salt may be used and the front face of a semiconductor particle may be processed. As desirable amines, a pyridine, a 4-t-butyl pyridine, a polyvinyl pyridine, etc. are mentioned. As the desirable 4th class salt, TETORO butyl ammonium iodide, tetrapod hexyl ammonium iodide, etc. are mentioned. When these are liquids, it may use as it is, and you may dissolve and use for an organic solvent.

[0118] (C) A charge transporting-bed charge transporting bed is a layer containing the charge transportation material which has the function to supplement the oxidant of coloring matter with an electron. the solution (electrolytic solution) which the ion of a redox couple dissolved as an ion-transport material as an example of a typical charge transportation material which can be used for this charge transporting bed, the so-called gel electrolyte which sank the solution of a redox couple into the gel of a polymer matrix, and the quality of molten salt electrolysis containing a oxidation reduction counter ion -- a solid electrolyte is mentioned further Moreover, although the electrolyte constituent of this invention is used for this charge transporting bed other than the charge transportation material with which ion is concerned at this invention, the above-mentioned charge transportation material other than this can also be used together.

[0119] (C-1) Two kinds of methods can be considered about the formation method of the formation charge transporting bed of a charge transporting bed. One is the method of sticking a counter electrode previously on a photosensitive layer, and putting a liquefied charge transporting bed between the gap. Another is the method of giving a charge transporting bed directly on a photosensitive layer, and a counter electrode will be given after that.

[0120] In the case of the former, the ordinary-pressure process which uses the capillarity by being immersed etc. as how to put a charge transporting bed, or the vacuum process which makes it a pressure lower than an ordinary pressure, and replaces the gaseous phase of a gap by the liquid phase

can be used.
[0121] In the case of the latter, in a wet charge transporting bed, a counter electrode will be given with not drying, and the liquid disclosure prevention measure of the edge section will be taken. Moreover, in the case of a gel electrolyte, there is a method of applying with wet and solidifying by methods, such as a polymerization, and a counter electrode can also be given after drying and fixing in that case. As a method of giving a gel electrolyte besides the electrolytic solution, the same method as grant of the above-mentioned semiconductor particle layer or coloring matter can be used.
[0122] (D) Like the aforementioned conductive base material, the monolayer structure of a counter electrode conductive layer which consists of a conductive material is sufficient as a counter electrode counter electrode, and it may consist of a counter electrode conductive layer and a support substrate. As electric conduction material used for a counter electrode conductive layer, a metal, carbon (for example, platinum, gold, silver, copper, aluminum, magnesium, an indium, etc.), or conductive metallic oxides (an indium-tin multiple oxide, fluorine dope tin oxide, etc.) are mentioned. Also in this, platinum, gold, silver, copper, aluminum, and magnesium can be preferably used as a counter electrode layer. As an example of the desirable support substrate of a counter electrode, it is glass or plastics, and vacuum evaporationo is applied or carried out and the above-mentioned electric conduction agent is used for this. Although especially the thickness of a counter electrode conductive layer is not restricted, 3nm - 10 micrometers are desirable. The surface electrical resistance of a counter electrode layer is so good that it is low. As a range of desirable surface electrical resistance, it is below 50ohms / **, and they are below 20ohms / ** still more preferably.
[0123] Since light may be irradiated from both a conductive base material, and both [either or], in order for light to reach a photosensitive layer, it is good if at least one side of a conductive base material and a counter electrode is substantially transparent. It is desirable to make a conductive base material transparent from a viewpoint of improvement in a generating efficiency, and to carry out incidence of the light from a conductive base material side. In this case, as for a counter electrode, it is desirable to have the property to reflect light. As such a counter electrode, the glass which deposited the metal or the conductive oxide, plastics, or a metal thin film can be used.
[0124] A counter electrode should just stick the application, plating, or conductive-layer side of the substrate which carries out vacuum evaporationo (PVD, CVD), or has a conductive layer for direct electric conduction material on a charge transporting bed. Moreover, as well as the case of a conductive base material when especially a counter electrode is transparent, it is desirable to use a metal lead in order to lower resistance of a counter electrode. In addition, the fall of the desirable quality of the material of a metal lead and the desirable installation method, and the amount of incident lights by metal lead installation etc. is the same as the case of a conductive base material.
[0125] (E) In order to prevent other layer counter electrodes and the short circuit of a conductive base material, beforehand, it is desirable to paint the thin film layer of a conductive base material and a semiconductor precise between photosensitive layers as an under coat, and especially when using electronic transportation material and electron hole transportation material for a charge transporting bed, it is effective. As an under coat, TiO2, SnO2, Fe 2O3, and WO3, ZnO and Nb 2O5 are desirable, and TiO2 is more desirable. An under coat is Electrochim. Acta 40 It can paint by the spatter besides the spray pyrolysis method indicated by 643-652 (1995) etc. The thickness of an under coat has desirable 5-1000nm or less, and its 10-500nm is more desirable.
[0126] Moreover, you may prepare functional layers, such as a protective layer and an acid-resisting layer, between one side of the conductive base material which acts as an electrode, and a counter electrode or both outside front faces, a conductive layer, and substrates, or in the middle of a substrate. According to the quality of the material, the applying method, a vacuum deposition, the sticking method, etc. can be used for formation of these functional layers.
[0127] In order to prevent said degradation of each structure and vaporization of contents, as for the photoelectrochemical cell of this invention, it is desirable to seal the side with polymer, adhesives, etc.

[0128] The photoelectrochemical cell of this invention is the same composition as the aforementioned optoelectric transducer. fundamentally, it connects the aforementioned optoelectric transducer to an external circuit through lead wire etc., and it constitutes it so that it may be made to work in an external circuit. The external circuit itself connected to the aforementioned conductive base material and the aforementioned counter electrode through lead wire etc. can use a well-known thing. Moreover, the photoelectrochemical cell of this invention can take the same module structure as fundamentally as the conventional solar cell module. Although the structure of a cell being constituted on support substrates, such as a metal and a ceramic, and the aforementioned solar cell module covering a it top with a restoration resin, cover glass, etc. generally, and incorporating light from the opposite side of a support substrate is taken, it is also possible to consider as the structure of using transparent materials, such as tempered glass, for a support substrate, constituting a cell on it, and incorporating light from the transparent support substrate side. The substrate one apparatus module structure specifically used with the module structure called a super straight type, a substrate type, and potting type, an amorphous-silicon solar cell, etc. is known, and the photoelectrochemical cell of this invention can also choose such module structures suitably according to the purpose of use, a service space, and environment. Specifically, it is desirable to apply the structure and the mode of a publication to the specification of JP,2000-268892,A.

[0129] The non-water rechargeable battery of this invention which used the electrolyte constituent of this invention below for the <non-water rechargeable battery> is explained. The non-water rechargeable battery of this invention is characterized by including the electrolyte constituent of this invention. The non-water rechargeable battery of this invention shows the outstanding cycle nature, without reducing capacity greatly, since the electrolyte constituent of this invention is contained.

[0130] - When using the electrolyte constituent of a positive-electrode active-substance-this invention for a non-water rechargeable battery, although the transition-metals oxide which can insert and emit a lithium ion in reversible is sufficient as a positive active material, its lithium content transition-metals oxide is especially desirable.

[0131] In this invention, an oxide including the lithium content Ti, V, Cr, Mn, Fe, Co, nickel, Cu, Mo, and W is suitably mentioned as a lithium content transition-metals oxide positive active material preferably used as a positive-electrode active substance. Moreover, you may mix alkali metal other than a lithium (element of the 1st (IA) group of a periodic table, and the 2nd (IIA) group), aluminum, Ga, In, germanium, Sn, Pb, Sb, Bi, Si, P, B, etc. 0-30-mol% of the amount of mixtures is desirable to transition metals.

[0132] What was mixed and compounded also in the quality of a lithium content transition-metals oxide preferably used as the aforementioned positive-electrode active substance so that the mole ratio of the sum total of a lithium compound / transition-metals compound (at least one sort chosen from Ti, V, Cr, Mn, Fe, Co, nickel, Mo, and W with transition metals here) might be set to 0.3-2.2 is more desirable.

[0133] Moreover, what was mixed and compounded also in the aforementioned lithium compound / transition-metals compound so that the mole ratio of the sum total of a lithium compound / transition-metals compound (at least one sort chosen from V, Cr, Mn, Fe, Co, and nickel with transition metals here) might be set to 0.3-2.2 is especially desirable.

[0134] Furthermore, the material containing LigM 3O2 (one or more sorts, g=0-1.2 as which M3 is chosen from Co, nickel, Fe, and Mn), or the material which has the Spinel structure expressed with LihM 42O4 (M4 is Mn and h=0-2) is especially desirable also in the aforementioned lithium compound / transition-metals compound. As the above M3 and M4, you may mix aluminum, Ga, In, germanium, Sn, Pb, Sb, Bi, Si, P, or B in addition to transition metals. 0-30-mol% of the amount of mixtures is desirable to transition metals.

[0135] LigCoO2, LigNiO2, LigMnO2, LigCojNi(1-j) O2, and LihMn 2O4 (here, it is h= 0.1 to 0:9, g=0.02-1.2, and j=0.1-0.9) are the most desirable also in material including the above LigM 3O2, and the material which has the Spinel structure expressed with LihM 42O4. Here, the above-mentioned g

value is a value before a charge-and-discharge start, and is fluctuated by charge and discharge.
[0136] Although the aforementioned positive active material is compoundable by well-known methods, such as the method of mixing a lithium compound and a transition-metals compound and calcinating, and a solution reaction, especially its calcinating method is desirable.
[0137] the non-water rechargeable battery of this invention -- setting -- business -- **** -- the above -- a positive active material -- although especially average grain size is not limited, its 0.1-50 micrometers are desirable Although not limited especially as a specific surface area, 0.01-50m2/g is desirable at a BET adsorption method. Moreover, as pH of the supernatant when melting 5g of positive active materials to 100ml of distilled water, 12 or less [7 or more] are desirable.
[0138] In order to make the aforementioned positive active material into a predetermined grain size, the grinder and classifier which were known well are used. For example, a mortar, a ball mill, a vibration ball mill, a vibration mill, a satellite ball mill, a planet ball mill, a revolution air current type jet mill, a screen, etc. are used. After washing by water, acid solution, alkaline solution, and the organic solvent, you may use the positive active material obtained by the aforementioned calcinating method.
[0139] - In the non-water rechargeable battery of a negative-electrode active-substance-this invention, the carbonaceous material in which occlusion discharge of a lithium is possible is suitably mentioned as one of the negative-electrode active materials. The aforementioned carbonaceous material is a material which consists of carbon substantially. For example, the carbonaceous material which calcinated various kinds of synthetic resin, such as artificial graphites, such as a petroleum pitch, a natural graphite, and a vapor-growth graphite, and a resin of a PAN system, and a furfuryl alcohol resin, can be mentioned. Furthermore, various carbon fibers, such as a PAN system carbon fiber, a cellulose system carbon fiber, a pitch based carbon fiber, a vapor-growth carbon fiber, a dehydration PVA system carbon fiber, a lignin carbon fiber, a vitrified carbon fiber, and an activated carbon fiber, a mesophase microsphere, a graphite whisker, a plate-like graphite, etc. can also be mentioned.
[0140] Such carbonaceous material can also be divided into difficulty graphitized-carbon material and a graphite system carbon material according to the grade of graphitization. Moreover, as for carbonaceous material, it is desirable to have the spacing indicated by JP,62-22066,A, JP,2-6856,A, and the 3-45473 official report, density, and the size of a microcrystal. Carbonaceous material does not need to be a single material and the graphite which has the mixture of a natural graphite and an artificial graphite given in JP,5-90844,A and an enveloping layer given in JP,6-4516,A can also be used for it.
[0141] In the non-water rechargeable battery of this invention, an oxide and/or chalcogenide are suitably mentioned as another negative-electrode active material used.
[0142] Also in it, an amorphous oxide and/or chalcogenide are desirable especially. It is the object which has the broadcloth dispersion band which has the peak to a 20 to 40 degrees field with 2theta value with the X-ray diffraction method ["be / amorphous / it"] here using CuK alpha rays, and you may have a crystalline diffraction line. It is desirable that the strongest intensity is 100 or less times of the diffraction line intensity of the peak of the broadcloth dispersion band looked at by 20 degrees or more 40 degrees or less with 2theta value among the crystalline diffraction lines looked at by 40 degrees or more 70 degrees or less with 2theta value, and especially the thing for which that they are 5 or less times does not have a more desirable crystalline diffraction line is desirable.
[0143] Also in the aforementioned amorphous oxide and/or chalcogenide, the amorphous oxide of a semimetal element and/or chalcogenide are more desirable, and the element of the 13th (IIIB) group of a periodic table - 15 (VB) groups, independent or the oxide which consists of two or more sorts of those combination of aluminum, Ga, Si, Sn, germanium, Pb, Sb, and Bi, and especially chalcogenide are desirable.
[0144] the above -- as a desirable amorphous oxide and/or chalcogenide For example, Ga 2O3, SiO, GeO, SnO, SnO2, PbO, PbO2, Pb 2O3, Pb2O4, Pb3O4, Sb2O3, Sb2O4, Sb2O5, Bi2O3, Bi2O4, SnSiO3, GeS, SnS, SnS2, PbS and PbS2, Sb2S3, Sb2S5, SnSiS3, etc. are desirable. Moreover, these

may be the multiple oxides 2 with a lithium oxide, for example, Li2SnO.
[0145] as the negative-electrode active substance used for the non-water rechargeable battery of this invention -- the above -- the amorphous oxide consisting mainly of Sn, Si, and germanium is still more desirable in a desirable amorphous oxide and/or desirable chalcogenide, and it is desirable that it is especially the amorphous oxide expressed with the following general formula (VI) also in it
[0146] General formula (VI)
SnM1dM2eOf[0147] in the aforementioned general formula (VI), M1 is chosen from aluminum, B, P, and germanium -- at least -- the element more than a kind, and M2 -- the [periodic-table] -- it is chosen out of 1(IA) group element, the 2nd (IIA) group element, the 3rd (IIIA) group element, and a halogen -- the element more than a kind is expressed at least 0.2 or more numbers [two or less] and e express 0.2<d+e<2 with or more 0.01 one or less number, and, as for d, f expresses or more 1 six or less number.
[0148] Although the example (C-1 to C-18) of the amorphous oxide which makes Sn a subject is shown below, this invention is not limited to these.
[0149]
C-1 SnSiO3 C-2 Sn0.8Al0.2B0.3P0.2Si0.5O3.6 C-3 SnAl0.4B0.5Cs0.1P0.5O3.65 C-4 SnAl0.4B0.5Mg0.1P0.5O3.7 C-5 SnAl0.4B0.4Ba0.08P0.4O3.28 C-6 SnAl0.4B0.5Ba0.08Mg0.08P0.3O3.26 C-7 SnAl0.1B0.2Ca0.1P0.1Si [0.5O3.1] C-8 SnAl0.2B0.4Si 0.4O2.7 C-9 SnAl0.2B0.1Mg0.1P0.1Si 0.5O2.6 C-10 SnAl0.3B0.4P0.2Si 0.5O3.55 C-11 SnAl0.3B0.4P0.5Si 0.5O4.3 C-12 SnAl0.1B0.1P0.3Si 0.6O3.25 C-13 SnAl0.1B0.1Ba0.2P0.1Si 0.6O2.95 C-14 SnAl0.1B0.1calcium0.2P0.1Si 0.6O2.95 C-15 SnAl0.4B0.2Mg0.1Si 0.6O3.2 C-16 SnAl0.1B0.3P0.1Si 0.5O3.05 C-17 SnB0.1K0.5P0.1SiO3.65 C-18 SnB0.5F0.1Mg0.1P0.5O3.05
[0150] Although any method of the calcinating method and a solution method can be used for the amorphous oxide and/or cull scorch night of this invention, its calcinating method is more desirable. After often mixing the oxide, cull scorch night, or compound of the element which corresponds, respectively by the aforementioned calcinating method, it is desirable to calcinate and to obtain an amorphous oxide and/or a cull scorch night. These are already producible by the well-known method.

[0151] In the non-water rechargeable battery of this invention, the average grain size of the aforementioned negative-electrode active substance used has desirable 0.1-60 micrometers. In order to make it a predetermined grain size, the grinder and classifier which were known well are used. For example, a mortar, a ball mill, a sand mill, a vibration ball mill, a satellite ball mill, a planet ball mill, a revolution air current type jet mill, a screen, etc. are used. At the time of pulverization, wet grinding which made organic solvents, such as water or a methanol, live together can also be performed if needed. It is desirable to perform a classification in order to consider as a desired particle size. As the classification method, there is especially no limitation and it can use a screen, a pneumatic elutriation machine, etc. if needed. Dry type and wet can be used for a classification.
[0152] As a negative-electrode active substance which can be combined and can be used for the amorphous oxide negative-electrode active substance centering on Sn, Si, and germanium of this invention, the metal in which occlusion, the carbon material which can be emitted, a lithium and a lithium alloy, and a lithium and an alloy are possible is suitably mentioned in a lithium ion or a lithium metal.
[0153] - an electrode -- a mixture -- the electrode of - this invention -- as a mixture, the non-proton nature organic solvent else [, such as an electric conduction agent, a binder, and a filler,] is added
[0154] In the constituted cell, if the aforementioned electric conduction agent is an electronic-conduction nature material which does not cause a chemical change, it is good anything. Usually, conductive material, such as natural graphites (a flaky graphite, a scale-like graphite, earthy graphite, etc.), an artificial graphite, carbon black, acetylene black, KETCHIEN black, a carbon fiber, and metal powders (copper, nickel, aluminum, silver (JP,63-148,554,A), etc.), a metal fiber or a polyphenylene derivative (JP,59-20,971,A), can be included as one sort or such mixture. Especially

combined use of a graphite and acetylene black is desirable. As an addition of the aforementioned electric conduction agent, 1 - 50 mass % is desirable, and 2 - 30 mass % is more desirable. Especially in the case of carbon or a graphite, 2 - 15 mass % is desirable.

[0155] this invention -- an electrode -- the binder for holding a mixture can be used As an example of the aforementioned binder, the polymer which has polysaccharide, thermoplastics, and rubber elasticity is mentioned. As a desirable binder, starch, a carboxymethyl cellulose, A cellulose, a diacetyl cellulose, a methyl cellulose, a hydroxyethyl cellulose, Hydroxypropylcellulose, alginic-acid Na, a polyacrylic acid, Polyacrylic-acid Na, a polyvinyl phenol, a polyvinyl methyl ether, Polyvinyl alcohol, a polyvinyl pyrrolidone, a polyacrylonitrile, Water-soluble polymer, such as a polyacrylamide, PORIHIDOROKISHI (meta) acrylate, and a styrene-maleic-acid copolymer, Polyvinyl chloride, a polytetrafluoroethylene, a polyvinylidene fluoride, A tetrapod FURORO ethylene-hexa FURORO propylene copolymer, a vinylidene fluoride-tetrapod FURORO ethylene-hexa FURORO propylene copolymer, Polyethylene, polypropylene, an ethylene-propylene-diene terpolymer (EPDM), Sulfonation EPDM, a polyvinyl-acetal resin, a methylmetaacrylate, The acrylic-ester (meta) copolymer containing acrylic esters (meta), such as 2-ethylhexyl acrylate The polyvinyl ester copolymer containing vinyl esters, such as an acrylic-ester-acrylonitrile copolymer and vinyl acetate, (Meta) A styrene-butadiene copolymer, an acrylonitrile-butadiene copolymer, A polybutadiene, neoprene rubber, a fluororubber, a polyethylene oxide, An emulsion (latex) or suspensions, such as a polyester polyurethane resin, a polyether polyurethane resin, a polycarbonate polyurethane resin, polyester resin, phenol resin, and an epoxy resin, can be mentioned. Especially, the latex of a polyacrylic ester system, a carboxymethyl cellulose, polytetrafluoroethylene, and a polyvinylidene fluoride are mentioned.

[0156] the aforementioned binder is independent -- or it can mix and use if there are few additions of a binder -- an electrode -- the holding power and cohesive force of a mixture are weak If many [too], electrode volume will increase and an electrode unit volume or the capacity per unit mass will decrease. Since it is such, the addition of a binder has desirable 1 - 30 mass %, and its 2 - 10 mass % is especially desirable.

[0157] The aforementioned filler can be used anything, if it is the fibrous material which does not cause a chemical change in the constituted cell. Usually, fiber, such as olefin system polymer, such as polypropylene and polyethylene, glass, and carbon, is used. Although especially the addition of a filler is not limited, 0 - 30 mass % is desirable.

[0158] - The electrolyte constituent of a separator-this invention can be used for safety reservation, using together with a separator. The separator used together for safety reservation needs to have the function which blockades the above-mentioned crevice above 80 degrees C, raises resistance, and intercepts current, and it is desirable that lock out temperature is 90 degrees C or more and 180 degrees C or less.

[0159] The configurations of the hole of the aforementioned separator are usually a round shape and an ellipse form, a size is 0.05 micrometers to 30 micrometers, and 0.1 to its 20 micrometers are desirable. Furthermore, you may be the hole of the shape of a rod, or an indeterminate form like [at the time of making by the extending method and the phase separation method]. It is 20% to 90%, the ratio, i.e., the porosity, which these crevices occupy, and it is desirable. [35 to 80% of]

[0160] Even if the aforementioned separators are single material, such as polyethylene and polypropylene, they may be two or more sorts of composite-ized material. What carried out the laminating of two or more sorts of fine porosity films into which an aperture, porosity, the lock out temperature of a hole, etc. were changed is especially desirable.

[0161] - The electronic-conduction object which does not cause a chemical change in the constituted cell as a charge collector of charge collector-positive and a negative electrode is used.

[0162] As a charge collector of a positive electrode, the thing which made the front face of aluminum or stainless steel else [, such as aluminum, stainless steel, nickel and titanium,] process carbon, nickel, titanium, or silver is desirable, and aluminum and an aluminium alloy are more desirable.

[0163] As a charge collector of a negative electrode, copper, stainless steel, nickel, and titanium are desirable, and copper or especially a copper alloy is desirable.
[0164] Although a film sheet-like thing is usually used, what was netted and punched, a lath object, a porosity object, a foam, the Plastic solid of a fiber group, etc. can be used for the configuration of the aforementioned charge collector. Although especially the thickness of the aforementioned charge collector is not limited, its 1-500 micrometers are desirable. Moreover, as for a current collection body surface, it is also desirable to attach irregularity with surface treatment.
[0165] - Explain creation of the non-water rechargeable battery of this invention below to creation - of a non-water rechargeable battery. As a configuration of the non-water rechargeable battery of this invention, a sheet, an angle, a cylinder, etc. are applicable to all. On a charge collector, the mixture of a positive active material or negative-electrode material is applied, (coat) dried and compressed, and is mainly used.
[0166] the above -- as the method of application of a mixture, the reverse rolling method, the direct rolling method, the blade method, the knife method, the extrusion method, the curtain method, the gravure method, the bar method, the dipping method, and the squeeze method can be mentioned, for example The blade method, the knife method, and the extrusion method are desirable also in it. Moreover, as for an application, it is desirable to carry out the speed for 0.1-100m/. Under the present circumstances, according to the solution physical properties of a mixture, and a drying property, the surface state of a good application layer can be obtained by selecting the above-mentioned method of application. You may perform an application to double-sided **** also in the time of one side [every] **.
[0167] Furthermore, continuation, intermittence, or a stripe is sufficient as the aforementioned application. Although the thickness, length, and width of the application layer are decided with the configuration and size of a cell, the thickness of the application layer of one side is in the state where it was compressed after dry, and its 1-2000 micrometers are desirable.
[0168] Dryness of the aforementioned electrode sheet application object and the dehydration method can carry out the thing of hot blast, a vacuum, infrared radiation, far infrared rays, an electron ray, and the damp wind using independent or the combined method. The range of drying temperature of 80-350 degrees C is desirable, and its range which is 100-250 degrees C is especially desirable. moisture content -- the cell whole -- 2000 ppm or less -- desirable -- a positive electrode -- a mixture and a negative electrode -- it is desirable to make it 500 ppm or less in a mixture or an electrolyte, respectively Although the method generally adopted can be used for the method of pressing a sheet, especially its calender pressing method is desirable. Although especially press ** is not limited, its 0.2 - 3 t/cm2 is desirable. The press speed of the calender pressing method has the amount of desirable 0.1-50m/, and press temperature has desirable room temperature -200 degree C. As for the ratio of negative-electrode sheet width of face to a positive-electrode sheet, 0.9-1.1 are desirable, and 0.95-especially 1.0 are desirable. the content ratio of a positive active material and negative-electrode material -- a compound kind and a mixture -- it changes with prescription
[0169] After processing it into a sheet-like cell as it is after piling up the positive and negative electrode sheet created by the aforementioned method through a separator, or bending, it inserts in a square shape can, and after connecting a sheet with a can electrically, the electrolyte constituent of this invention is poured in and it forms using an obturation board.
[0170] Moreover, after inserting in a cylinder-like can after piling up and rolling a positive and negative electrode sheet through a separator, and connecting a sheet with a can electrically, the electrolyte constituent of this invention is poured in and a cylinder cell is formed using an obturation board. At this time, a relief valve can be used as an obturation board. It may be equipped with the various safe elements known from the former besides a relief valve. For example, a fuse, bimetal, a PTC element, etc. are suitably used as an overcurrent-protection element.
[0171] Moreover, the method of making a cut in a cell can, the gasket crack method, the obturation board crack method, or cutting process with a lead board can be used for everything but a relief valve

as a cure of an internal pressure rise of a cell can. Moreover, the protection network which built the surcharge and the cure against an overdischarge into the battery charger may be made to provide, or you may make it connect independently.

[0172] Moreover, the method which intercepts current by the rise of cell internal pressure can be provided as a cure against overcharge. At this time, the compound which raises internal pressure can be included in a mixture or an electrolyte. as the example of the compound used in order to raise internal pressure -- Li2 -- carbonates, such as CO3, LiHCO3, Na2CO3, and NaHCO3, CaCO3, MgCO3, etc. can be mentioned

[0173] A metal and an alloy with electrical conductivity can be used as a can or a lead board. For example, metals or those alloys, such as iron, nickel, titanium, chromium, molybdenum, copper, and aluminum, are used suitably.

[0174] As a welding process of a cap, a can, a sheet, and a lead board, a well-known method (electric welding of an example, a direct current, or an alternating current, laser welding, ultrasonic welding) can be used. As a sealing compound for obturation, the compound and mixture which are known from the former, such as asphalt, can be used.

[0175] Although especially the use of the non-water rechargeable battery of this invention is not limited, when it carries in electronic equipment, for example, A notebook computer, pen input personal computer, mobile personal computer, and Electronic Book player, a cellular phone and a cordless phon -- a cordless handset, a pager, and a handy terminal -- Pocket facsimile, a pocket copy, a pocket printer, a headphone stereo, A video movie, a liquid crystal television, a handy cleaner, portable CD, a mini disc, an electric shaver, a transceiver, an electronic notebook, a calculator, memory card, a pocket tape recorder, radio, a backup power supply, memory card, etc. are mentioned. In addition, as a noncommercial use, an automobile, electric vehicles, a motor, lighting fitting, a toy, a game machine machine, a load conditioner, a clock, a stroboscope, a camera, medical equipment (a pacemaker, a hearing-aid, shoulder Japanese fir machine, etc.), etc. are mentioned. Furthermore, it can use as the various objects for munitions, and an object for space. Moreover, it is also combinable with a solar battery.

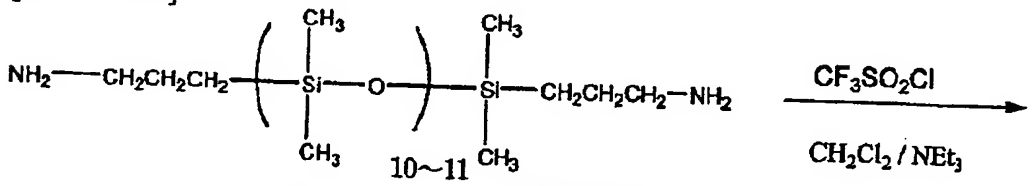
[0176]

[Example] Hereafter, although an example explains this invention concretely, this invention is not limited at all by these examples.

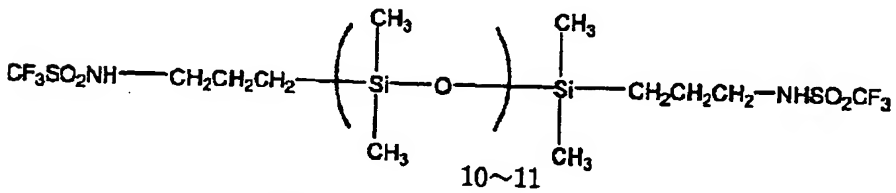
[0177] (Example 1) Synthetic (1) instantiation compound P-1 of a compound, and composition of P-2

[0178]

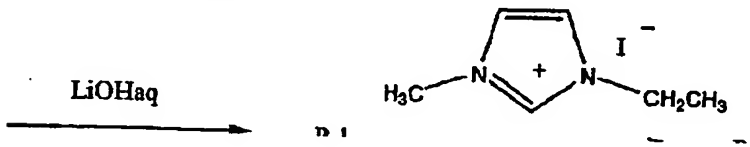
[Formula 26]



M-1 平均分子量９００－１０００



M-2



P-1 ⟶ P-2

[0179] ** After dissolving synthetic diamine (M-1) 18g of intermediate field M-2 in 50ml of methylene chlorides and adding truffe RUORO sulfonyl chloride 8.4g, it was dropped at -30 degrees C, having triethylamine 7 bet it for about 10 minutes. Under the room temperature, after stirring for 3 hours, 30ml of water was added to reaction mixture, liquid separation and 1-N hydrochloric-acid water washed the methylene-chloride phase, and reduced pressure distilling off of the methylene chloride was carried out after dryness with magnesium sulfate. The concentrate was refined in silica gel column chromatography (methylene chloride), and M-2 [10g] was obtained as oily matter.
[0180] ** Disulfon amide (M-2) 10g obtained by the synthetic above of P-1 was dissolved in THF50ml, 2O0.7g of LiOH-H and 5ml of water were added, and heating reflux was carried out for 30 minutes. Magnesium sulfate was added and filtered to reaction mixture, the methylene chloride was added for the filtrate after reduced pressure distilling off, reduced pressure distilling off of the filtrate which filtered insoluble matter was carried out again, and P-1 [6.0g] was obtained as colorless oily matter after dryness with the vacuum dryer. The structure check was performed by H1NMR and the methyl group on Si and the proton ratio of CH2CH2CH2 showed that it was the average 10 of n (average molecular weight 1192).
[0181] ** 5.0g (P-1) of synthetic screw lithium imide salts of P-2 was distributed in 20ml of methylene chlorides, and 20ml of water, iodation 1-ethyl-4-methyl imidazolium 2.0g was added, and it stirred for room temperature-ized 30 minutes. The methylene-chloride phase was separated and it condensed after rinsing. The concentrate was refined in silica gel column chromatography, and P-2 [5.5g] was obtained as colorless oily matter.
[0182] (Example 2) The manufacture inside of photoelectrochemical-cell 2-1. titanium-dioxide dispersion liquid to the vessel made from stainless steel of 200ml of content volume which carried out Teflon (registered trademark) coating 15g (Degussamade from Japanese Aerosil P-25) of titanium dioxides, 45g of water, With 1g [of dispersants] (Aldrich make, Triton X-100) and a diameter of 0.5mm zirconia-beads (Nikkato Corp. make) 30g was put in, and it distributed in 1500rpm for 2 hours using the Sand-grinder mill (product made from eye MEKKUSU). Zirconia beads were filtered and removed from the distributed object. The mean particle diameter of the titanium dioxide in this case was 2.5 micrometers. The particle size at this time is measured in the master sizer made from MALVERN.
[0183] 2-2. The glass rod was used and the above-mentioned dispersion liquid were applied to the electric conduction side side of the electrically conductive glass (what carried out cutting processing of the TCO glass [by Asahi Glass Co., Ltd.]-U at the 20mmx20mm size) which coated the tin oxide which doped the creation fluorine of TiO2 electrode (electrode A) which adsorbed coloring matter. Under the present circumstances, the adhesive tape was stretched to the part by the side of an electric conduction side (from an edge to 3mm), and it considered as the spacer, and glass was put in order and it applied eight sheets at a time at once so that an adhesive tape might come to ends. After the application, it exfoliated and the adhesive tape was air-dried for one day at the room temperature. Next, this glass was put into the electric furnace (muffle furnace FP-32 type made from Yamato Science), and it calcinated for 30 minutes at 450 degrees C. It flooded with the ethanol solution (3xten - four mols/(l.)) of coloring matter R-1 for 3 hours, after taking out this glass and cooling. After being immersed in a 4-tert-butyl pyridine for 15 minutes, the air drying of the glass which coloring matter dyed was washed and carried out by ethanol. Thus, the thickness of the photosensitive layer obtained is 10 micrometers, and the coverage of a semiconductor particle was taken as 20 g/m2. In addition, the surface electrical resistance of electrically conductive glass was about 30ohm/**.
[0184] 2-3. The acetonitrile was distilled off, applying the acetonitrile solution (an acetonitrile being a constituent and a homogeneous amount) of the electrolyte constituent (E-102 to E-110) containing the compound or comparison compound of this invention shown in Table 1 to the TiO2 electrode substrate (1cmx1cm) which is the creation **** of a photoelectrochemical cell, and was made and

created and by which the color sensitizing was carried out, and infiltrating it into TiO2 electrode under 60 degrees C and reduced pressure. The platinum vacuum evaporationo glass of the same size was laid on top of these electrodes, and the photoelectrochemical cell (sample B-102 to B-110) was obtained (Table 1, drawing 2). Moreover, after laying the electrolytic solution (E-101 of Table 1) using the solvent on top of the same TiO2 electrode substrate (2cmx2cm) as the above by which coloring matter sensitization was carried out with the platinum vacuum evaporationo glass of the same size as the electrode, it infiltrated the electrolytic solution into the crevice between both glass using capillarity, and created the photoelectrochemical cell (sample B-101). In addition, the cell (B-110) using the electrolyte E-110 containing the salt P-31 which has a polymerization nature machine performed heating at 80 degrees C after cell creation for 1 hour in order to carry out the polymerization of the electrolyte.

[0185] The photoelectrochemical cell by which the laminating of electrically conductive glass 1 (that by which the electric conduction agent layer 2 was ****(ed) on glass), TiO2 electrode 3, a pigment layer 4, an electrolyte 5, the platinum layer 6, and the glass 7 was carried out to order was created by this example as shown in drawing 2 .

[0186]

[Table 1]

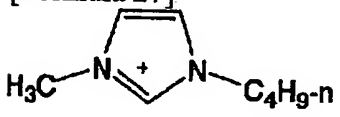
電解質	組成（質量%）	サンプル	備考
E-101	RE-1 (48) /BCE (50) /I2 (2)	B-101	比較例
E-102	RE-1 (98) /I_2 (2)	B-102	比較例
E-103	RE-1 (48) /RE-2 (50) / I_2 (2)	B-103	比較例
E-104	RE-1 (48) /P-2 (50) / I_2 (2)	B-104	本発明
E-105	RE-1 (48) /P-3 (50) / I_2 (2)	B-105	本発明
E-106	RE-1 (48) /P-6 (50) / I_2 (2)	B-106	本発明
E-107	RE-1 (48) /P-10 (50) / I_2 (2)	B-107	本発明
E-108	RE-1 (48) /P-14 (50) / I_2 (2)	B-108	本発明
E-109	RE-1 (48) /P-21 (50) / I_2 (2)	B-109	本発明
E-110	RE-1 (48) /P-31 (48) / I_2 (2) /AIBN	B-110	本発明

BCE（溶媒）：ビスシアノエチルエーテル

AIBN（熱重合開始剤）：アゾイソブチロニトリル

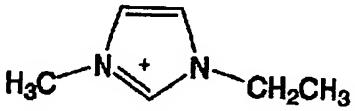
[0187]

[Formula 27]



I^-

RE-1



$^-N(SO_3CF_3)_2$

RE-2

[0188] 2-4. It is AM1.5 about the light of the xenon lamp of measurement 500W of a photoelectric conversion efficiency (USHIO make). By letting a filter (product made from Oriel), and a sharp cut filter (KenkoL-41) pass, the simulation sunlight which does not include ultraviolet rays was generated and this luminous intensity was adjusted to 100 mW/cm2.

[0189] The crocodile clip was connected to the above-mentioned electrically conductive glass and above-mentioned platinum vacuum evaporationo glass of a photoelectrochemical cell, respectively, and the electrical and electric equipment which irradiated simulation sunlight and was generated at 45 degrees C was measured in the current-potential measuring device (case rhe SMU238 type). the open circuit voltage (Voc) of the photoelectrochemical cell called for by this, short-circuit current density (Jsc), and a form factor -- (FF) [= maximum output/(open-circuit-voltage x short-circuit current)] and a conversion efficiency (eta), and constant temperature -- the decreasing rate of the short-circuit

current density after carrying out the passage of time for 400 hours was collectively indicated to Table 2 under constant humidity (60 degrees C, 70%R.H.)

[0190]

[Table 2]

サンプル	J c s (mA/m²)	Voc (V)	FF	η (%)	Jsc低下率(%) 60℃－湿度70% 400時間	備考
B-101	10.1	0.66	0.64	4.3	99	比較例
B-102	7.8	0.6	0.65	3.0	11	比較例
B-103	9.2	0.64	0.68	4.0	21	比較例
B-104	11.1	0.65	0.67	4.8	5	本発明
B-105	10.6	0.64	0.68	4.6	7	本発明
B-106	10.5	0.67	0.65	4.6	8	本発明
B-107	12.1	0.64	0.64	5.0	8	本発明
B-108	10.6	0.65	0.64	4.4	6	本発明
B-109	9.9	0.64	0.68	4.3	7	本発明
B-110	9.5	0.68	0.62	4.0	4	本発明

Jsc：短絡電流密度、Voc：開放電圧、FF：形状因子、η：変換効率

[0191] Since a solvent volatilizes, the photoelectrochemical cell (B-101) using the comparison electrolytic solution using the solvent has very bad endurance. Moreover, the comparison sample (B-102, B-103) using fused salt RE-1 and/or RE-2 passes, and although degradation in the time is small, a photo-electric-translation performance is not enough [degradation]. When the salt of this invention is used to them, initial performances, such as short-circuit current density and a conversion efficiency, and endurance are excellent. Such an effect was seen when which coloring matter was used.

[0192] (Example 3) As a creation positive active material of a lithium rechargeable battery 3-1. positive-electrode sheet LiCoO2 43 mass sections, the scale-like graphite 2 mass section, the acetylene black 2 mass section, Furthermore, add the polyacrylonitrile 3 mass section as a binder, and the slurry which kneaded the acrylonitrile 100 mass section as a medium, and was obtained is painted on an aluminum foil with a thickness of 20 micrometers using an extrusion formula application machine. After pressing with the calender press machine after dryness, the lead board made from aluminum was welded to the edge, and the positive-electrode sheet with 95 micrometers [in thickness] and a width-of-face [of 54mm] x length of 49mm was created.

[0193] 3-2. as the creation negative-electrode active material of a negative-electrode sheet -- a meso face pitch system carbon material (PETOKA) -- as 43 mass sections and an electric conduction agent -- the acetylene black 2 mass section and the graphite 2 mass section -- comparatively -- coming out -- mixing -- further -- as a binder -- a polyacrylonitrile -- 3 mass sections -- adding -- the N-methyl pyrrolidone 100 mass section -- as a medium -- kneading -- a negative electrode -- a mixture -- the slurry was obtained a negative electrode -- a mixture -- the slurry was painted on copper foil with a thickness of 10 micrometers using the extrusion formula application machine, it pressed with the calender press machine after dryness, and the negative-electrode sheet with 46 micrometers [in thickness] and a width-of-face [of 55mm] x length of 50mm was created After welding the lead board made from nickel to the edge of a negative-electrode sheet, it heat-treated at 230 degrees C for 1 hour in dry air of -40 degrees C or less of dew-points. Heat treatment was performed using the far-infrared heater.

[0194] The creation negative-electrode sheet of a 3-3. sheet cell and the positive-electrode sheet carried out dehydration dryness at 230 degrees C for 30 minutes in dry air of -40 degrees C or less of dew-points, respectively. In dry atmosphere, the laminating of the separator (polyethylene porosity film) and nonwoven fabric which were judged in a dried [dehydration] positive-electrode sheet with a width-of-face [of 54mm] x length of 49mm and width-of-face [of 60mm] x length of 60mm was

carried out, the liquid which dissolved the electrolyte (E-202-213) of the composition shown in Table 3 in the acetonitrile of the amount of said was applied on the nonwoven fabric, and the acetonitrile was distilled off under reduced pressure at 50 degrees C. Moreover, the electrolytic solution (E-201) using the solvent was infiltrated into the nonwoven fabric as it is. The laminating of the dried [dehydration] negative-electrode sheet with a width-of-face [of 55mm] x length of 50mm was carried out on it, using the sheathing material which consists of a laminate film of a polyethylene (50 micrometers)-polyethylene terephthalate (50 micrometers), heat weld was carried out, four edges were sealed under the vacuum, and the sheet type cell (B-201 to B-213) was created. In addition, the cell (B-209) using the electrolyte E-209 containing the salt P-30 which has a polymerization nature machine performed heating at 80 degrees C after cell creation for 1 hour in order to carry out the polymerization of the electrolyte. The composition of the sheet cell created by this example is shown in drawing 3 .

[0195]

[Table 3]

電解質番号	電解質組成（質量%）	電池番号	備考
E-201	RE-3 (30) /PC (30) /EC (40)	B-201	比較例
E-202	RE-3 (30) /RE-2 (70)	B-202	比較例
E-203	$LiBF_4$ (30) /RE-2 (70)	B-203	比較例
E-204	P-1 (100)	B-204	本発明
E-205	P-5 (100)	B-205	本発明
E-206	P-9 (100)	B-206	本発明
E-207	P-13 (100)	B-207	本発明
E-208	P-18 (100)	B-208	本発明
E-209	P-30 (98) /AIBN (2)	B-209	本発明
E-210	P-1 (30) /RE-3	B-210	本発明
E-211	P-5 (30) /RE-3	B-211	本発明
E-212	P-1 (30) /PEO	B-212	本発明
E-213	P-5 (30) /PEO	B-213	本発明

PC：プロピレンカーボネート

EC：エチレンカーボネート

RE-3 : $LiN(SO_2CF_3)_2$

PEO : $-(CH_2CH_2O)_n-$ (平均分子量 3000)

[0196] 3-4. About the sheet type cell created by the evaluation aforementioned method of a cell performance, charge and discharge were repeated 30 times on condition that current density 1.3 mA/cm2, charge final-voltage 4.2V, and discharge-final-voltage 2.6V**, and the service capacity in 30 cycle eye was calculated. This was investigated about five cells of the same prescription, and the average was made into the capacity of the cell. Thus, the capacity of each cell was calculated and the relative capacitor to SB-1 was calculated. Moreover, the service capacity of a 200 cycle eye was calculated about each cell, the ratio to the service capacity of 10 cycle eye was calculated, and it expressed as a cycle capacity. Each value was shown in Table 4.

[0197]

[Table 4]

電池番号	相対容量	サイクル容量	備考
B-201	1	0.28	比較例
B-202	0.61	0.87	比較例
B-203	0.33	0.78	比較例
B-204	0.84	0.98	本発明
B-205	0.72	0.95	本発明
B-206	0.81	0.96	本発明
B-207	0.85	0.98	本発明
B-208	0.94	0.95	本発明

B-209	0.66	0.95	本発明
B-210	0.95	0.94	本発明
B-211	0.91	0.94	本発明
B-212	0.93	0.93	本発明
B-213	0.90	0.95	本発明

[0198] The above-mentioned result shows that the electrolyte constituent of this invention is raising cycle nature, without seeing the big fall of capacity.

[0199]

[Effect of the Invention] The new electrolyte constituent containing the new polysiloxane salt and this salt which according to this invention did not volatilize substantially and were excellent in electrification transportation ability is offered, and the electrochemical cell which was excellent in endurance and ion conductivity including this electrolyte constituent, the photoelectrochemical cell excellent in endurance and the optical transfer characteristic, and cell capacity cannot be reduced further, and it can offer offering the non-water rechargeable battery which was moreover excellent in the cycle property.

[Translation done.]

* NOTICES *

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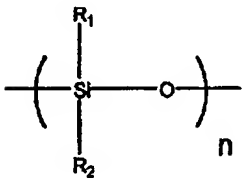
TECHNICAL FIELD

[The technical field to which invention belongs] this invention relates to the electrochemical cell using the electrolyte constituent which contains a cell, a new suitable as other electrochemistry device material polysiloxane salt (an "electrolyte salt" may be called below), and the salt concerned in more detail, and the electrolyte constituent concerned especially a nonaqueous electrolyte rechargeable battery, and a photoelectrochemical cell about a polysiloxane salt, an electrolyte constituent, an electrochemical cell, a non-water rechargeable battery, and a photoelectrochemical cell.

[Translation done.]

Drawing selection [Representative drawing]



一般式（１）

[Translation done.]

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PRIOR ART

[Description of the Prior Art] The electrolyte used for electrochemical cells, such as a non-water rechargeable battery and a coloring matter sensitization solar battery, is a medium which has the function (it is called ionic conduction) to convey the ion to inter-electrode, including the ion according to the purpose. For example, with the lithium secondary battery which is the representation of a non-water rechargeable battery, the conductivity of iodine ion and iodine trimer ion poses [transportation of a lithium ion] a problem by the coloring matter sensitization solar battery. In these cells, generally, although many solution systems with high ion conductivity are used as an electrolyte, there is a problem of an exhaustion of the solvent at the time of including in a cell and leakage reducing the endurance of a cell. That is, when the electrolyte which used the common low-molecular solvent is built into a cell, there is a problem that the cell performance by volatilization of a solvent or the liquid spill deteriorates. Moreover, in order to seal a solution in a lithium secondary battery, a metal vessel must be used, cell mass becomes heavy, and there is a problem that it is difficult to also give flexibility to a cell configuration.

[0003] In order to conquer the fault of the aforementioned solution system electrolyte, various electrolytes are proposed in recent years. although the fall of ionic conductivity does not drop a cell performance small to a solution system electrolyte, the so-called gel electrolyte which made the solution electrolyte permeate a polymer matrix has the problem obtained and said, if volatilization of a solvent cannot be inhibited completely Moreover, although the polymer electrolyte which dissolved the salt in polymer, such as a polyethylene oxide, is expected as what solves the problem of a solution system electrolyte, it has the problem that ionic conductivity is not yet enough.

[0004] On the other hand, although the method using the so-called quality of molten salt electrolysis which used the salt of a liquid as the base at the room temperature is learned, since a low-boiling point compound is not included, while it is effective in preventing degradation of the cell performance by volatilization, since viscosity is high, generally there is a problem of a low in charge transportation ability. For example, although an opposite anion is room temperature fused salt with imidazolium salts and pyridinium salts liquefied at a room temperature, such as BF4- and 2 (CF3SO2)N-, and it is proposed as an electrolyte for lithium ion batteries, an electrolytic mechanical strength and ion conductivity conflict, and when own viscosity of fused salt was raised, or it is the means of making polymer contain etc. and a mechanical strength is strengthened, the fall of ionic conductivity is seen. Furthermore, in the above electrolytes, ion conductivity temperature dependence is large and there is a problem that especially the ion conductivity in low temperature is inadequate.

[0005] By the way, although compound solar batteries, such as a single-crystal-silicon solar battery, a polycrystal silicon solar cell, an amorphous-silicon solar cell, a cadmium telluride, and selenium-ized indium copper, are set as the object of utilization or research and development, the photovoltaics which transform a light energy into electrical energy need to conquer troubles, such as reservation of a manufacturing cost and raw material, and the length of an energy pay back time, when making it spread. On the other hand, although many solar batteries using the organic material which pointed to large-area-izing or low-pricing are also proposed until now, a conversion efficiency is low and there is a problem that endurance is also bad.

[0006] In such a situation, the technology of a photoelectrochemical cell using the optoelectric transducer (it abbreviates to a coloring matter sensitization optoelectric transducer henceforth) using the oxide semiconductor by which sensitization was carried out to Nature (the 353rd volume, the

737-740th page, 1991), U.S. JP,4927721,B, etc. with coloring matter, and this was indicated. This cell consists of the optoelectric transducer, charge transfer layer, and counter electrode which function as a negative electrode. An optoelectric transducer consists of a conductive base material and a photosensitive layer, and a photosensitive layer contains the semiconductor with which coloring matter stuck to the front face. A charge transfer layer consists of a oxidation reduction object, and bears charge transportation between a negative electrode and a counter electrode (positive electrode). In the photoelectrochemical cell proposed by the above-mentioned patent, the solution (electrolytic solution) which uses salts, such as potassium iodide, as an electrolyte as a charge transfer layer was used. This method is cheap and it is a problem for a photoelectric conversion efficiency not to fall remarkably by evapotranspiration of the electrolytic solution and exhaustion, if it is used over a long period of time, although it is promising, or to stop functioning as a cell in that a comparatively high energy conversion efficiency (photoelectric conversion efficiency) is obtained.

[0007] The method of using as an electrolyte the imidazolium salt which is a low melting point compound as the exhaustion prevention method of the electrolytic solution at WO 95/No. 18456 is indicated to such a problem. Since according to this method water and the organic solvent which were used as an electrolytic solvent were unnecessary or little and ended conventionally, although the improvement of endurance was found, endurance is still inadequate. Moreover, when the imidazolium salt was made into high concentration, while viscosity became high, charge transportation ability fell, and there was a problem that a photoelectric conversion efficiency became low. Furthermore, there is the method of using a thoria ZORIUMU salt as an electrolyte, and there is the same problem as an imidazolium salt also in this method.

[0008] In order to conquer the fault of a solution system electrolyte also in the electrolyte used for electrochemical cells, such as a non-water rechargeable battery, the electrolytic solid state (polymer electrolyte) is studied in recent years. Although the polymer electrolyte which dissolved the salt in polymer, such as a polyethylene oxide, is expected as what solves the problem of a solution system electrolyte, ionic conductivity is not yet enough. Moreover, generally the ion transference number (in the case of a lithium secondary battery, it is the lithium ion transference number) which is one of the important electrolytic properties in the polymer electrolyte mainly reported so far is a low. therefore -- for example, the actual condition is that it is difficult to include in the goods with which a charge and discharge current decreases with time, and causes problems, such as causing the fall of capacity, and with which in the case of a lithium secondary battery it is flexible

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[Translation done.]

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EFFECT OF THE INVENTION

[Effect of the Invention] The new electrolyte constituent containing the new polysiloxane salt and this salt which according to this invention did not volatilize substantially and were excellent in electrification transportation ability is offered, and the electrochemical cell which was excellent in endurance and ion conductivity including this electrolyte constituent, the photoelectrochemical cell excellent in endurance and the optical transfer characteristic, and cell capacity cannot be reduced further, and it can offer offering the non-water rechargeable battery which was moreover excellent in the cycle property.

[Translation done.]

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] this invention solves the problem in the aforementioned former, and makes it a technical problem to attain the following purposes. Namely, this invention offers the new electrolyte constituent containing the new polysiloxane salt and this salt which did not volatilize substantially and were excellent in electrification transportation ability, does not reduce further the electrochemical cell which was excellent in endurance and ion conductivity including this electrolyte constituent, the photoelectrochemical cell excellent in endurance and the optical transfer characteristic, and cell capacity, and aims at offering the non-water rechargeable battery which was moreover excellent in the cycle property.

[Translation done.]

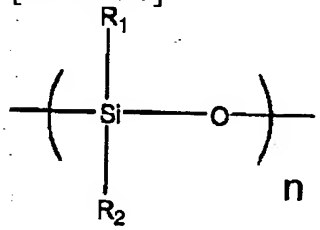
MEANS

[Means for Solving the Problem] The aforementioned The means for solving a technical problem is as follows.

<1> It is the electrolyte constituent characterized by containing the salt which has in structure the anion section which a proton comes to dissociate from at least one among the atomic group expressed with the following general formula (I), a sulfonamide and disulfon imide, N-acyl sulfonamide, alcohol, a phenol, and a sulfonic acid, and the cation section which is the metal ion and/or the organic cation belonging to the 1st group of a periodic table, or the 2nd group.

[0011]

[Formula 7]



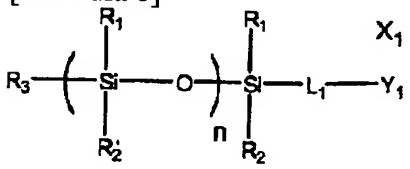
一般式（Ｉ）

[0012] In the aforementioned general formula (I), R1 and R2 express an alkyl group, an aryl group, or an alkoxy group. n expresses three or more numbers.

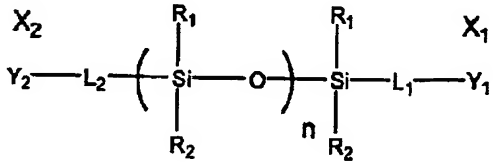
[0013] <2> The aforementioned salt is an electrolyte constituent given in the above <1> which is the salt expressed with the structure of either the following general formula (III-a) and the following general formula (III-b).

[0014]

[Formula 8]



一般式(III-a)



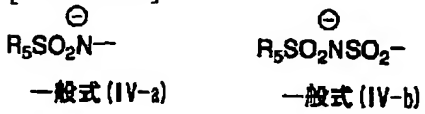
一般式(III-b)

[0015] In the aforementioned general formula (III-a) and the aforementioned general formula (III-b), R1 and R2 express an alkyl group independently respectively. X1 and X2 express the aforementioned cation section independently respectively. Even if X1 and X2 are mutually the same, they may differ. L1 and L2 express the divalent connection machine containing the alkylene machine. Y1 and Y2 express the substituent containing the aforementioned anion section. Even if Y1 and Y2 are mutually the same, they may differ. R3 expresses the alkyl group which is not replaced [substitution or]. n expresses three or more numbers.

[0016] <3> The above R1 and R2 is the alkyl groups of the carbon atomic numbers 1-3. It is the divalent connection machine by which the above L1 and L2 is respectively expressed independently

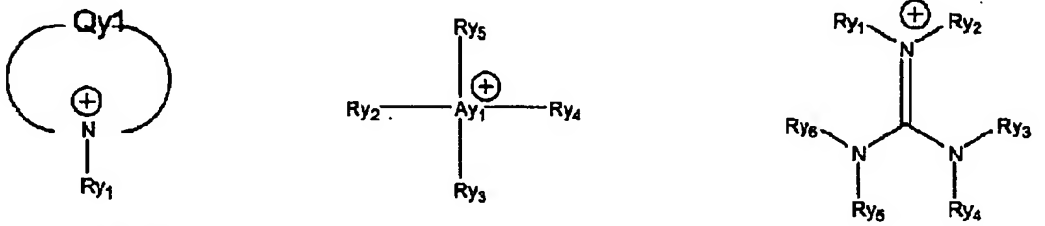
with either -(CH2) 3- and -(CH2) 3OCH2CH2-. Y1 and Y2 are the above <1> which is a substituent containing the anion section respectively expressed with the structure of either the following general formula (IV-a) and a general formula (IV-b) independently, or an electrolyte constituent given in <2>.

[0017]
[Formula 9]



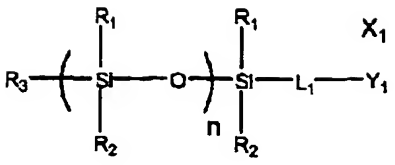
一般式(IV-a)　一般式(IV-b)

[0018] In the aforementioned general formula (IV-a) and a general formula (IV-b), R5 expresses the alkyl group of the carbon atomic numbers 1-3.
[0019] <4> The aforementioned cation section is an electrolyte constituent given in either of <3> from the above <1> which is a lithium ion.
[0020] <5> The aforementioned cation section is an electrolyte constituent given in either of <3> from the above <1> which is either among the cation sections expressed with a general formula (II-a), a general formula (II-b), and a general formula (II-c).
[0021]
[Formula 10]

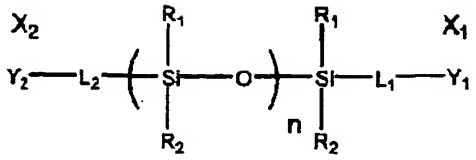


一般式(II-a)　一般式(II-b)　一般式(II-c)

[0022] In the aforementioned general formula (II-a), Qy1 expresses the atomic group which can form the aromatic cation of 5 member rings or 6 member rings with a nitrogen atom. Ry1 expresses the alkyl group or alkenyl machine which is not replaced [substitution or]. In the aforementioned general formula (II-b), Ay1 expresses a nitrogen atom or the Lynn atom. Ry1, Ry2, Ry3, and Ry4 express the alkenyl machine which is not replaced [the alkyl group which is not replaced / substitution or /, substitution, or]. Moreover, two or more may form the un-aromatic ring which connects mutually and contains Ay1 among Ry1, Ry2, Ry3, and Ry4. In the aforementioned general formula (II-c), Ry1, Ry2, Ry3, Ry4, Ry5, and Ry6 may express the alkenyl machine which is not replaced [the alkyl group which is not replaced / substitution or /, substitution, or], among those two or more may connect them mutually, and they may form a ring structure. The compound expressed with the aforementioned general formula (II-a), a general formula (II-b), and a general formula (II-c) may form a polymer through Qy1, or Ry1-Ry6.
[0023] <6> It is the electrochemical cell characterized by including the electrolyte constituent of a publication in either of <5> from the above <1>.
[0024] <7> It is the non-water rechargeable battery characterized by including the electrolyte constituent of a publication in either of <5> from the above <1>.
[0025] <8> It is the photoelectrochemical cell characterized by having the charge transfer layer which contains the electrolyte constituent of a publication in either of <5> from the above <1>, a photosensitive layer containing the semiconductor by which sensitization was carried out with coloring matter, and a counterelectrode.
[0026] <9> It is the polysiloxane salt characterized by what is expressed with the structure of either the following general formula (III-a) and the following general formula (III-b).
[0027]
[Formula 11]



一般式(III-a)

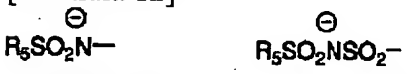


一般式(III-b)

[0028] In the aforementioned general formula (III-a) and the aforementioned general formula (III-b), R1 and R2 express the alkyl group of the carbon atomic numbers 1-3 independently respectively. X1 and X2 express a lithium ion. L1 and L2 express the binary connection machine respectively expressed with either -(CH2) 3- and -(CH2) 3OCH2CH2- independently. Y1 and Y2 express the substituent containing the anion section respectively expressed with the structure of either the following general formula (IV-a) and a general formula (IV-b) independently. R3 expresses the alkyl group which is not replaced [substitution or]. n expresses three or more numbers.

[0029]

[Formula 12]



一般式(IV-a)　　一般式(IV-b)

[0030] In the aforementioned general formula (IV-a) and a general formula (IV-b), R5 expresses the alkyl group of the carbon atomic numbers 1-3.

[0031]

[Embodiments of the Invention] Hereafter, the polysiloxane salt of this invention, an electrolyte constituent, an electrochemical cell, a non-water rechargeable battery, and a photoelectrochemical cell are explained. Here, the electrolyte constituent containing the polysiloxane salt and this salt of this invention is explained in detail first.

[0032] (A salt and electrolyte constituent) The electrolyte constituent of this invention is used for reaction solvents, such as a chemical reaction and metal plating, a CCD (charge-coupled device) camera, various electrochemical cells (the so-called cell), etc. It is more desirable for it to be preferably used for a non-water rechargeable battery (especially lithium secondary battery) or the photoelectrochemical cell using the following semiconductor, and to use for a photoelectrochemical cell.

[0033] The salt of this invention is characterized by having in structure the anion section which a proton comes to dissociate from at least one among the atomic group expressed with the aforementioned general formula (I), a sulfonamide and disulfon imide, N-acyl sulfonamide, alcohol, a phenol, or a sulfonic acid, and the cation section which is the metal ion and/or the organic cation belonging to the 1st group of a periodic table, or the 2nd group. The electrolyte constituent of this invention is characterized by being an electrolyte constituent containing the aforementioned salt.

[0034] The atomic group expressed with the aforementioned general formula (I) contained in the salt of a <atomic group expressed with general formula (I)> this invention is explained in full detail.

[0035] Carbon atomic numbers (Following more than C may be called) are 1-24 preferably. the aforementioned general formula (I) -- setting -- R1 and R2 -- each -- independent -- alkyl group [-- You may be branched-chain, even if it is more than C [1-10] more preferably and is a straight chain-like. For example, a methyl, ethyl, a propyl, butyl, i-propyl, i-butyl, A pentyl, a hexyl, an octyl, 2-ethylhexyl, t-octyl, A desyl, a dodecyl, tetradecyl, 2-hexyl desyl, hexadecyl, Octadecyl, cyclohexyl methyl, and octyl cyclohexyl], It is more than C [6-24] preferably, and is more than C [6-10] more preferably. aryl group [-- for example, phenyl and naphthyl] or alkoxy-group [-- more than C [1-24], for example, a methoxy, ethoxy ** butoxy, octyloxy, methoxyethoxy one, methoxy PENTA (ethyloxy), acryloyl oxyethoxy, and pentafluoro propoxy] are expressed preferably Furthermore, these [R1 and R2] may have the substituent. as a desirable substituent It is more than C [1-24] preferably, and is more than C [1-10] more preferably. alkyl group [which may be replaced -- You may be branched-chain even if it is a straight chain-like. For example, a methyl, ethyl, A propyl,

butyl, i-propyl, i-butyl, a pentyl, a hexyl, An octyl, 2-ethylhexyl, t-octyl, a desyl, a dodecyl, Tetradecyl, 2-hexyl desyl, hexadecyl one, octadecyl, cyclohexyl methyl and octyl cyclohexyl] and the aryl group (desirable -- more than C [6-24], for example, a phenyl, --) which may be condensing the ring even if it has replaced 4-methylphenyl, 3-cyano phenyl, 2-chlorophenyl, 2-naphthyl, the heterocycle machine that may be condensing the ring even if it has replaced (the nitrogen in a ring may form 4 class at the time of a nitrogen-containing heterocycle machine.) Preferably More than C [2-24], for example, 4-pyridyl, 2-pyridyl, 1-octyl pyridinium-4-IRU, 2-pyrimidyl, 2-imidazolyl, 2-thiazolyl, and alkoxy-group [-- desirable -- more than C [1-24], for example, a methoxy, -- Ethoxy ** butoxy, octyloxy, methoxyethoxy one, methoxy PENTA (ethyloxy), acryloyl oxyethoxy and pentafluoro propoxy] and an acyloxy machine (desirable -- more than C [1-24], for example, acetyloxy, --) benzoyloxy one and an alkoxy carbonyl group (desirable -- more than C [2-24], for example, a methoxycarbonyl, --) Ethoxycarbonyl, a cyano group, a fluoro machine, an alkoxy carbonyl group, a cyano group, and polymerization nature machines (preferably a vinyl group, an acryloyl machine, a methacryloyl machine, a styryl machine, a cinnamic acid residue, etc.) are mentioned. In the aforementioned general formula (I), n expresses three or more numbers.

[0036] The anion sections which constitute the salt of a <anion section> this invention are a sulfonamide, disulfon imide, N-acyl sulfonamide, alcohol, a phenol, and an anion which a proton comes to dissociate from at least one among sulfonic acids. As the aforementioned anion section, a sulfonamide, disulfon imide, and N-acyl sulfonamide are desirable.

[0037] As for the conjugate acid of the anion section, it is desirable that pKa is 11 or less, and it is more desirable that it is seven or less.

[0038] When the cation section which constitutes the salt of a <cation section> this invention is a metal ion belonging to a periodic table 1st (Ia) or the 2nd (IIa) group, unlike an oxy-alkylene machine, the atomic group shown by the general formula (I) does not interact with a cation strongly, but offers a flexible ionic conduction place from maneuverability being high. Thereby, the high ion transference number and high ion conductivity are realized.

[0039] As the cation section which constitutes the salt of this invention, the organic cation expressed with either the aforementioned general formula (II-a), the aforementioned general formula (II-b) and the aforementioned general formula (II-c) and/or a lithium ion are desirable.

[0040] In the aforementioned general formula (II-a), Qy1 expresses the atomic group which can form the aromatic cation of 5 member rings or 6 member rings with a nitrogen atom. Ry1 expresses the alkyl group or alkenyl machine which is not replaced [substitution or].

[0041] In the aforementioned general formula (II-b), Ay1 expresses a nitrogen atom or the Lynn atom. Ry1, Ry2, Ry3, and Ry4 express the alkyl group or alkenyl machine which is not replaced [substitution or]. Moreover, two or more of Ry1, Ry2, Ry3, and Ry4 may form the un-aromatic ring which connects mutually and contains Ay1.

[0042] In the aforementioned general formula (II-c), Ry1, Ry2, Ry3, Ry4, Ry5, and Ry6 may express the alkyl group or alkenyl machine which is not replaced [substitution or], among those two or more may connect them mutually, and they may form a ring structure.

[0043] The cation expressed with the aforementioned general formula (II-a), the aforementioned general formula (II-b), and the aforementioned general formula (II-c) may form a polymer through Qy1, or Ry1-Ry6.

[0044] aromatic [in nitrogen] in the aforementioned general formula (II-a) -- the composition atom of the atomic group Qy1 which can form the cation of 5 or 6 member ring is preferably chosen from carbon, hydrogen, nitrogen, oxygen, and sulfur

[0045] As 6 member rings completed by Qy1, it is a pyridine, a pyrimidine, a pyridazine, a pyrazine, and triazine, and is a pyridine more preferably.

[0046] As an aromatic 5 member ring completed by Qy1, it is an oxazole, a thiazole, an imidazole, a pyrazole, an isoxazole, thiadiazole, an OKISA diazole, and a triazole preferably, and they are an oxazole, a thiazole, and an imidazole more preferably. They are an oxazole and an imidazole especially preferably.

[0047] Setting to the aforementioned general formula (II-a), the aforementioned general formula (II-b), and the aforementioned general formula (II-c), Ry1-Ry6 are an alkyl group (even if carbon atomic

numbers (henceforth, more than C) are 1-24 preferably and it is a straight chain-like, it may be branched-chain, and you may be a ring type.) which is not replaced [substitution or]. For example, the ARUKENIRU machine which is not replaced [a methyl ethyl, a propyl, butyl, i-propyl, a pentyl, a hexyl, an octyl, 2-ethylhexyl, t-octyl, a desyl, a dodecyl, tetradecyl, 2-hexyl desyl, octadecyl, cyclohexyl, cyclopentyl, polymerization nature machines (preferably a vinyl group, an acryloyl machine, a methacryloyl machine, a styryl machine, a cinnamic acid residue, etc.), substitution, or] (you may be branched-chain, even if more than are 2- For example, a vinyl and an allyl compound are expressed, the alkyl group of more than C 3-18 or the ARUKENIRU machine of more than C 2-18 is expressed preferably, and the alkyl group of more than C 4-6 is expressed more preferably.

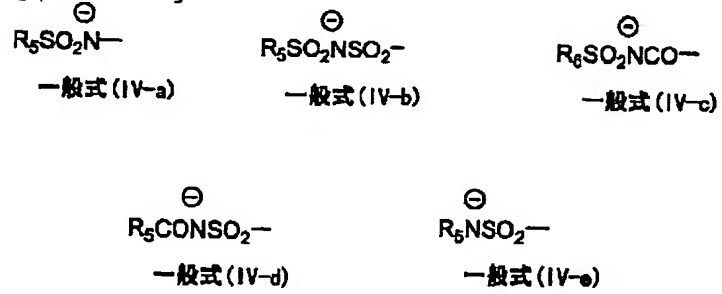
[0048] In the aforementioned general formula (II-a), the aforementioned general formula (II-b), and the aforementioned general formula (II-c), Qy1, and Ry1-Ry6 may have the substituent. As an example of a desirable substituent, a halogen atom (F, Cl, Br, I), A cyano group, an alkoxy group (a methoxy, ethoxy ** methoxyethoxy, etc.), aryloxy machines (phenoxy etc.) and an alkyl thio machine (a methylthio --) Acyl groups, such as an ethyl thio (an acetyl, a propionyl, benzoyl, etc.), a sulfonyl machine and an acyloxies (methane sulfonyl, benzenesulphonyl, etc.) machine (acetoxy --) Sulfonyloxy machine, such as benzoyloxy one (methane sulfo NIRIOKISHI) Phosphonyl groups, such as toluenesulfonyloxy (diethyl phosphonyl etc.), amide groups (acetylamino, benzoyl amide, etc.) and a carbamoyl group (N and N-dimethyl carbamoyl --) alkyl groups (a methyl, ethyl, and a propyl --), such as N-phenylcarbamoyl Aryl groups (a phenyl, toluyl, etc.), such as an isopropyl, a cyclo propyl, butyl, 2-carboxy ethyl, and a benzyl, heterocycle machines (for example, pyridyl, imidazolyl, furanyl, etc.), ARUKENIRU machines (a vinyl, 1-propenyl, etc.), etc. are mentioned.

[0049] The polysiloxane salt expressed with the aforementioned general formula (III-a) or the aforementioned general formula (III-b) is desirable as a salt of a <salt structure> this invention.

[0050] In the aforementioned general formula (III-a) and a general formula (III-b), R1 and R2 are the substituents and homonymy which were explained by the general formula (I). X1 and X2, and the cation section that ******(ed) are expressed, and even if these are the same, they may differ. L1 and L2 express the divalent connection machine containing the alkylene machine. Y1 and Y2 express the anion section mentioned above. Even if Y2 are the same as Y1, they may differ. R3 expresses the alkyl group which is not replaced [substitution or]. n expresses three or more numbers. In the aforementioned general formula (III-a) and the aforementioned general formula (III-b), the alkyl group which is not replaced [substitution or] is desirable as R1 and R2. As L1 and L2, a two or more-carbon number alkylene machine or an alkyleneoxy machine is desirable. As Y1 and Y2, the anion section expressed with a general formula (IV-e) from a general formula (IV-a) is desirable.

[0051]

[Formula 13]



[0052] R5 in a general formula (IV-e) expresses the alkyl group which is not replaced [substitution or], an aryl group, or a heterocycle machine from a general formula (I-Va).

[0053] As the alkyl group, aryl group, and heterocycle machine of R5, what was explained in full detail by R1 of the aforementioned general formula (I) is used preferably. Especially, in the case of the aforementioned general formula (IV-a) to the aforementioned general formula (IV-c), a fluorine substitution alkyl group is desirable, and a trifluoromethyl machine and a pentafluoro ethyl group are still more desirable to it. In the case of the aforementioned general formula (IV-d), the fluorine substitution alkyl group and the substitution, or the non-replaced phenyl group of more than C 1-5 is desirable. In the case of the aforementioned general formula (IV-e), the phenyl group which is not

replaced [substitution or] is desirable.

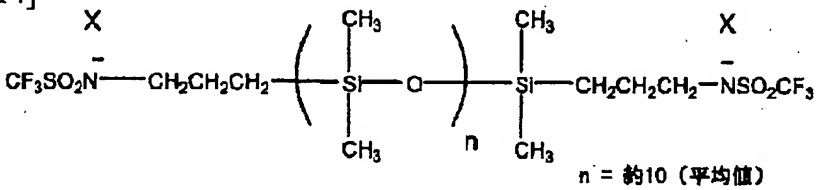
[0054] In the aforementioned general formula (III-a) and the aforementioned general formula (III-b), as for n, 3 to 30 is desirable, and 6 to 20 is more desirable.

[0055] Especially the desirable structure is as follows as a salt of this invention. Namely, it sets to the aforementioned general formula (III-a) or the aforementioned general formula (III-b). The above R1 and R2 is the alkyl groups of the carbon atomic numbers 1-3, and the above X1 and X2 is lithium ions. It is the divalent connection machine by which the above L1 and L2 is respectively expressed independently with either -(CH2) 3- and -(CH2) 3OCH2CH2-. Y1 and Y2 are the salts expressed with the structure which is a substituent containing the anion section respectively expressed with the structure of either the aforementioned general formula (IV-a) and the aforementioned general formula (IV-b) independently. In the aforementioned general formula (IV-a) and a general formula (IV-b), R5 expresses the alkyl group of the carbon atomic numbers 1-3.

[0056] Although the example of the salt which combined with below the anion structure of the salt used for the electrolyte constituent of this invention, cation structure, and them is shown, they cannot be combined arbitrarily and this invention is not necessarily limited to this.

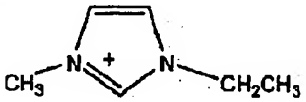
[0057]

[Formula 14]

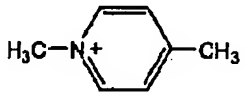


(P-1) X = Li^+

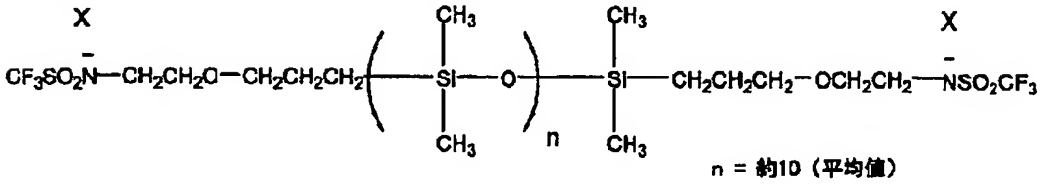
(P-2) X =



(P-3) X =

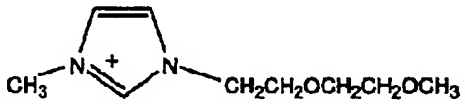


(P-4) X = $CH_3N^+(CH_2CH_3)_3$

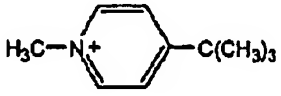


(P-5) X = Li^+

(P-6) X =



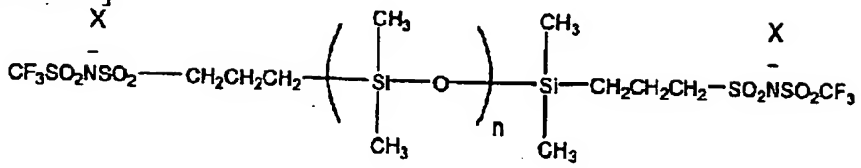
(P-7) X =



(P-8) X = $CF_3SO_2N^-Li^+$

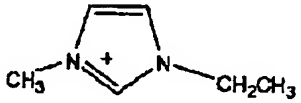
(P-8) X = $CH_3OCH_2CH_2N(CH_2CH_3)_3$

[0058]
[Formula 15]



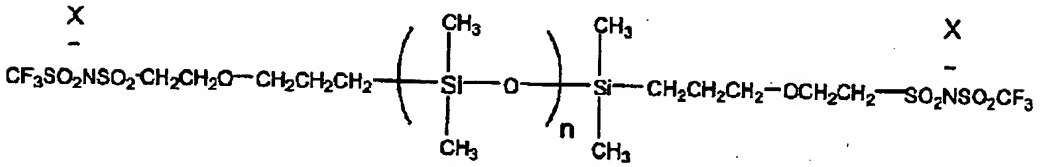
n=約10（平均値）

(P-9) X = Li^+

(P-10) X = 

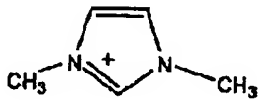
(P-11) X = 

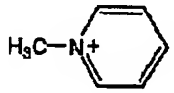
(P-12) X = $CH_3\overset{+}{N}(CH_2CH_3)_3$



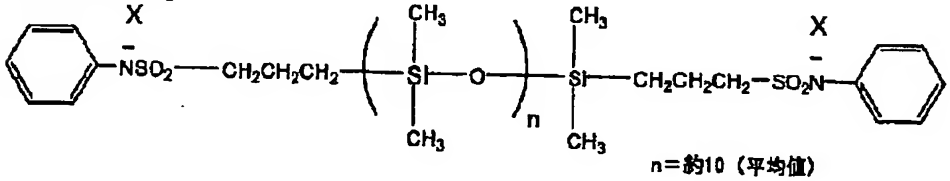
n=約30（平均値）

(P-13) X = Li^+

(P-14) X = 

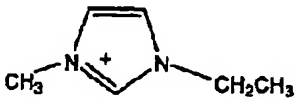
(P-15) X = 

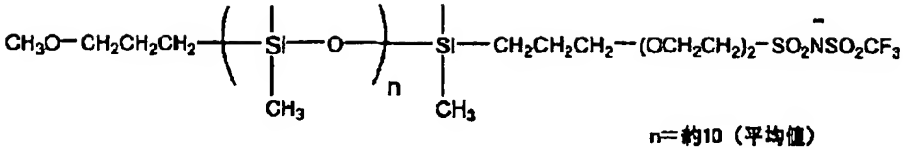
[0059]
[Formula 16]



n=約10（平均値）

(P-16) X = Li^+

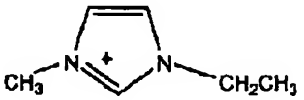
(P-17) X = 

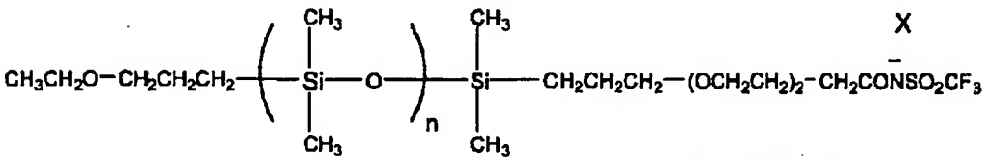


n＝約10（平均値）

(P-18) X = Li^+

(P-19) X =

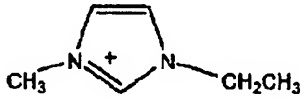




n＝約30（平均値）

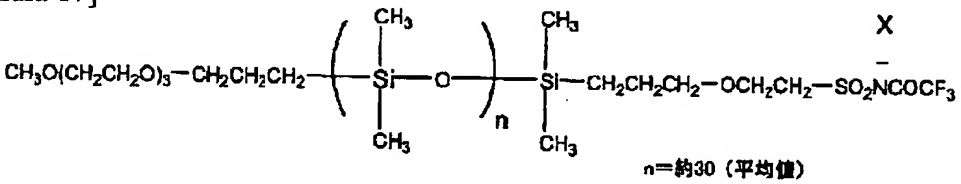
(P-20) X = Li^+

(P-21) X =



[0060]

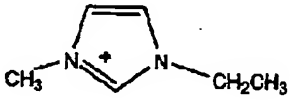
[Formula 17]

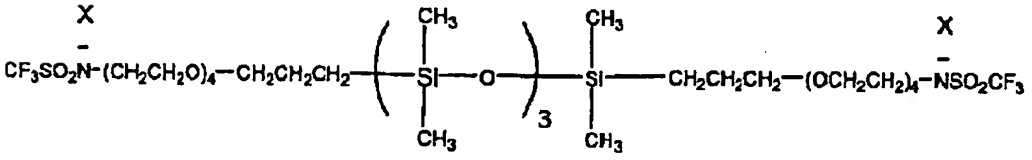


n＝約30（平均値）

(P-22) X = Li^+

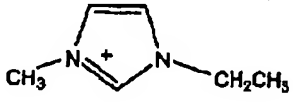
(P-23) X =



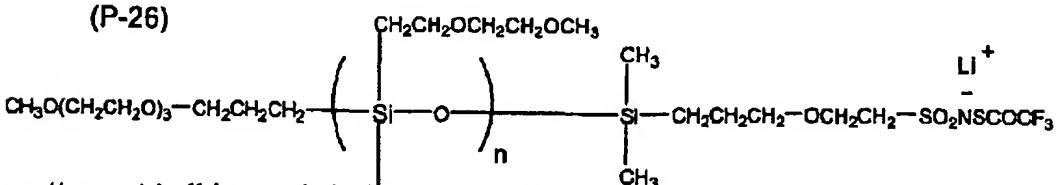


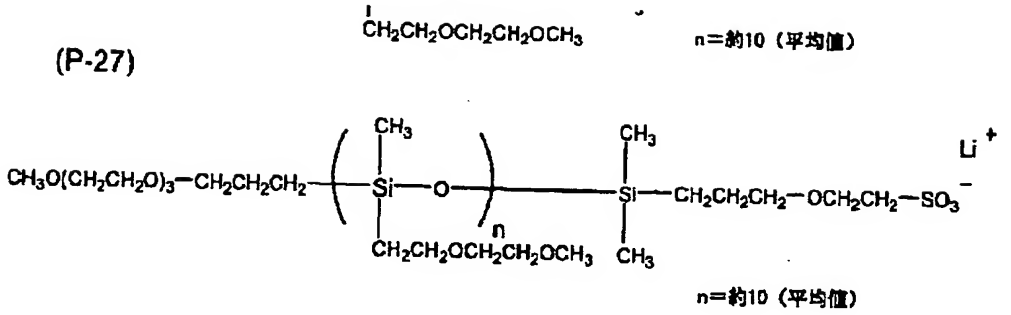
(P-24) X = Li^+

(P-25) X =



(P-26)



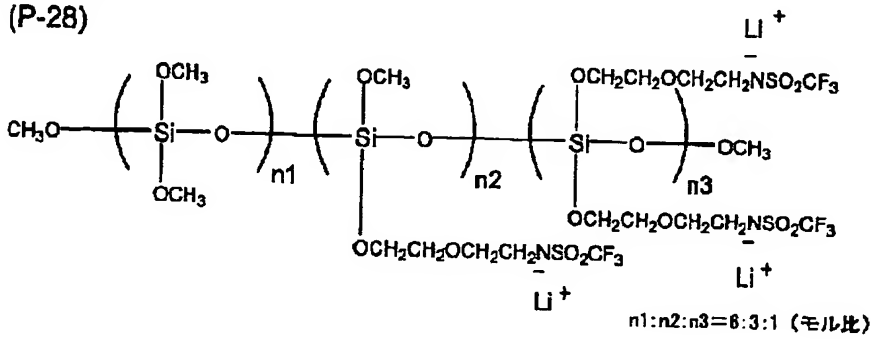


(P-27)

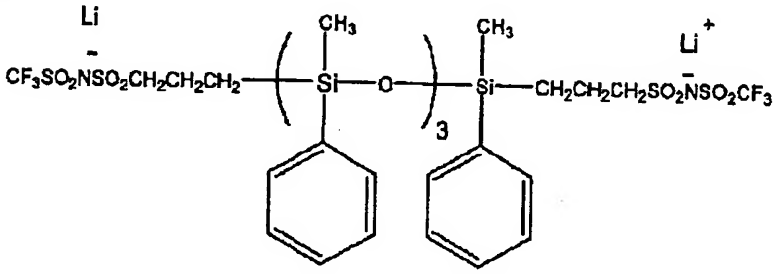
[0061]

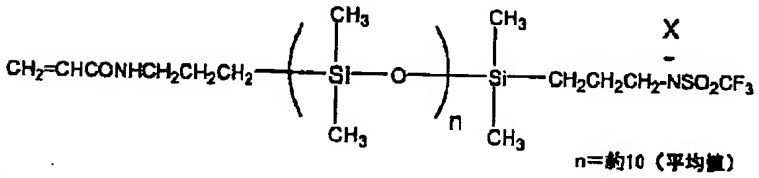
[Formula 18]

(P-28)



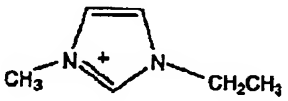
(P-29)



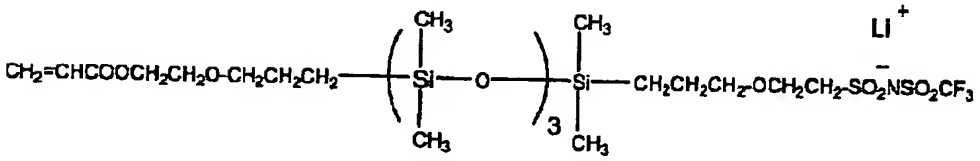


(P-30) X = Li^+

(P-31) X =

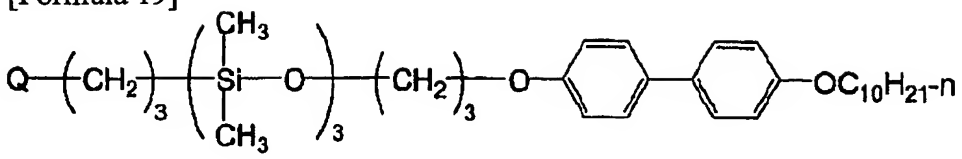


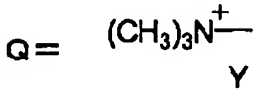
(P-32)



[0062]

[Formula 19]



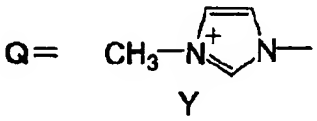


(P-33) Y = I^-

(P-34) Y = $^-N(SO_2CF_3)_2$

(P-35) Y = BF_4^-

(P-36) Y = $CF_3SO_3^-$

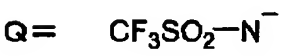


(P-37) Y = I^-

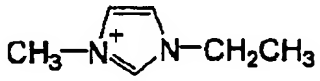
(P-38) Y = $^-N(SO_2CF_3)_2$

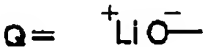
(P-39) Y = BF_4^-

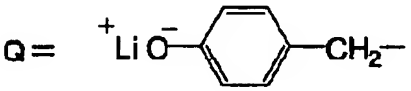
(P-40) Y = $CF_3SO_3^-$

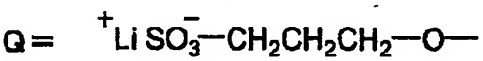


(P-41) Y = Li^+

(P-42) Y = 

(P-43) 

(P-44) 

(P-45) 

[0063] When using the electrolyte constituent of this invention for the electrolyte of a photoelectrochemical cell, it is desirable to use the electrolyte containing I- and I3- as a charge carrier, and it can add them in the form of arbitrary salts. As a desirable salt, YI- and YI3- mention, respectively and it is ****. Y is the cation section expressed with either the aforementioned general formula (II-a), the aforementioned general formula (II-b) and the aforementioned general formula (II-c) here. As for YI3-, it is common to add iodine (I2) to the bottom of YI-existence, and to make it generate in an electrolyte constituent. Added YI3- of I2 and the amount of said generates in that case.
[0064] Among the electrolyte constituent of this invention, the concentration of I- has desirable 10 - 90 mass %, and its 30 - 70 mass % is more desirable. It is desirable in that case that all the remaining components are the compounds of this invention expressed with a general formula (I).

[0065] It is more desirable that it is [0.1-20 mol] %, as for I3-, it is desirable that it is [0.1-50 mol / of I-] %, and it is / it is still more desirable that it is / 0.5-10 mol / %, and / most desirable that it is / 0.5-5 mol / %.

[0066] Still more nearly another fused salt may also be included in the electrolyte constituent of this invention. The fused salt used preferably combines the organic cation shown by the aforementioned general formula (II-a), the aforementioned general formula (II-b), and the aforementioned general formula (II-c), and arbitrary anions. As an anion, halogenide ion, SCN- (Cl-, Br-, etc.), BF4-, PF6-, ClO4-, 2 (CF3SO2)N-, 2 (CF3CF2SO2)N-, CH3SO3-, CF3SO3-, CF3COO-, Ph4B-, 3(CF3SO2) C-, etc. are mentioned as a desirable example, and it is more desirable that they are SCN-, CF3SO3-, CF3COO-, 2 (CF3SO2)N-, or BF4-. Moreover, alkali-metal salts, such as other iodine salts, such as LiI, CF3COOLi, CF3COONa, LiSCN, and NaSCN, can also be added. As for the addition of an alkali-metal salt, it is desirable that it is a 0.02 - 2 mass % grade, and its 0.1 - 1 mass % is still more desirable.

[0067] the electrolyte constituent of this invention -- LiI, NaI, KI, CsI, and CaI2 etc. -- a metal iodide -- The iodine salt of the 4th class imidazolium compound, the iodine salt of a tetraalkylammonium compound, Metal bromides, such as Br2, LiBr, NaBr, KBr, CsBr, and CaBr2, Or Br2 The bromine salt of the 4th class ammonium compounds, such as a tetrapod alkylammonium star's picture and a pyridinium star's picture Sulfur compounds, such as metal complexes, such as a ferrocyanic-acid salt-ferricyanic-acid salt and a ferrocene-ferricinium ion, the poly sodium sulfide, and alkyl thiol-alkyl disulfide, viologen coloring matter, a hydroquinone-quinone, etc. are made to contain, and can also be used. When making it contain, as for the amount of these compounds used, it is desirable that it is below 30 mass % of the whole electrolyte compound.

[0068] With the salt of this invention, a solvent can be preferably used to this compound and a homogeneous amount at the maximum.

[0069] As for the solvent used for the electrolyte of this invention, it is desirable for a dielectric constant to be high in improving ionic mobility low, and for viscosity to be the compound which improves effective carrier concentration and can discover the outstanding ion conductivity. As such a solvent, carbonate compounds, such as ethylene carbonate and propylene carbonate, Heterocyclic compounds, such as 3-methyl-2-oxazolidinone, a dioxane, Ether compounds, such as diethylether, ethylene glycol dialkyl ether, The propylene-glycol dialkyl ether, the polyethylene-glycol dialkyl ether, Chain-like ether, such as the polypropylene-glycol dialkyl ether, A methanol, ethanol, ethylene glycol monoalkyl ether, Propylene-glycol monoalkyl ether, polyethylene-glycol monoalkyl ether, Alcohols, such as polypropylene-glycol monoalkyl ether, Ethylene glycol, a propylene glycol, a polyethylene glycol, Polyhydric alcohol, such as a polypropylene glycol and a glycerol, an acetonitrile, Guru taro dinitrile, a methoxy acetonitrile, a propionitrile, Non-proton polar substances, such as ester, such as nitryl compounds, such as a benzonitrile, a carboxylate, phosphoric ester, and phosphonate, a dimethyl sulfoxide, and a sulfolane, water, etc. can be used. Also in this, nitryl compounds, such as heterocyclic compounds, such as carbonate compounds, such as ethylene carbonate and propylene carbonate, and 3-methyl-2-oxazolidinone, an acetonitrile, guru taro dinitrile, a methoxy acetonitrile, a propionitrile, and a benzonitrile, and especially ester are desirable. Even if it uses these independently, they may use two or more sorts together.

[0070] As a solvent, from a viewpoint of the improvement in endurance by volatility-proof, a thing 200 degrees C or more has the desirable boiling point in an ordinary pressure (one atmospheric pressure), a thing 250 degrees C or more is more desirable, and a thing 270 degrees C or more is still more desirable.

[0071] When using the electrolyte constituent of this invention for electrochemical cells, such as a lithium ion battery, it considers as the electrolyte constituent which added lithium salt. In this case, the anion of the lithium salt used An imido anion (CF3 SO2) (2 N-, 2 (CF3 CF2 SO2)N-) or boron (B), It is more desirable that they are the fluoride anions (BF4-, PF6-, CF3 SO3-, C(CF3SO2)3-, etc.) containing at least one or more kinds of elements chosen from Lynn (P) and sulfur (S). As concentration of the salt at that time, 1 mass % to 70 mass % is desirable to the compound of a general formula (I), and 20 mass % to 50 mass % is still more desirable.

[0072] (Electrochemical cell) The electrochemical cell of this invention is characterized for the

aforementioned electrolyte constituent of this invention by ******. As a mode of the electrochemical cell of this invention, a photoelectrochemical cell and a non-water rechargeable battery are mentioned.

[0073] The photoelectrochemical cell by which the electrolyte of this invention is preferably used below for a <photoelectrochemical cell> is explained. It enables it to use the photoelectrochemical cell of this invention for the cell use which makes an optoelectric transducer work in an external circuit, and it has the photosensitive layer and charge transfer layer containing the semiconductor which induces a radiant ray, and a counter electrode. The electrolyte constituent of this invention contains in this charge transfer layer.

[0074] The photoelectrochemical cell of this invention which used the electrolyte constituent of this invention for below is explained. The photoelectrochemical cell of this invention has the charge transporting bed containing the aforementioned electrolyte constituent, a photosensitive layer containing the semiconductor by which sensitization was carried out with coloring matter, and a counter electrode, and it constitutes them so that the optoelectric transducer explained to the so-called following may be made to work in an external circuit. The photoelectrochemical cell of this invention shows the outstanding endurance with small degradation of the cell performance in the passage of time while it is excellent in a photo-electric-translation performance, since the aforementioned charge transporting bed contains the electrolyte constituent of this invention.

[0075] - An example of an optoelectric transducer applicable to this invention at optoelectric-transducer- drawing 1 is shown. An optoelectric transducer 10 comes to carry out the laminating of a conductive layer 12, an under coat 14, a photosensitive layer 16, the charge transporting bed 18, and the counter electrode conductive layer 20 one by one. A photosensitive layer 16 turns into the semiconductor layer 24 which carried out sensitization with coloring matter d from the charge transportation material t. The semiconductor layer 24 is a porous layer which consists of a semiconductor particle s, the opening was formed between the semiconductor particles s and the charge transportation material t has permeated this opening. The charge transportation material t consists of the same component as the material used for the charge transporting bed 18. Under the conductive layer 12, the substrate 28 is arranged under the substrate 26 and the counter electrode conductive layer 20. Substrates 26 and 28 may be for giving intensity, and may not be in an optoelectric transducer. Moreover, on the boundary of each layer, for example, the boundary of a conductive layer 12 and a photosensitive layer 16, the boundary of a photosensitive layer 16 and the charge transporting bed 18, and the boundary of the charge transporting bed 18 and the counter electrode conductive layer 20, the constituents of each class may be carrying out diffusive mixing mutually. In addition, a conductive layer 12, a substrate 26, and/or the counter electrode conductive layer 20 and substrate 28 of the side which may carry out incidence of the light to an optoelectric transducer 10 from either or both sides, and carries out incidence of the light to it can consist of material which has light-transmission nature, respectively.

[0076] Next, an operation of an optoelectric transducer 10 is explained. In addition, the case where the semiconductor particle s is n type is explained. If light carries out incidence to an optoelectric transducer 10, the light which carried out incidence will reach a photosensitive layer 16, will be absorbed with coloring matter d etc., and will generate the coloring matter d of an excitation state. The excited coloring matter d passes the electron of a high energy to the conduction band of the semiconductor particle s, and it becomes an oxidant itself. The electron from which it moved to the aforementioned conduction band reaches a conductive layer 12 by the network of the semiconductor particle s. Therefore, a conductive layer 12 has an electronegative potential to the counter electrode conductive layer 20. In the mode which used the optoelectric transducer 10 for the photoelectric cell, if this photoelectric cell is connected with an external circuit, the electron in a conductive layer 12 will reach the counter electrode conductive layer 20, working in an external circuit. The generated reductant (for example, I3-) returns the oxidant of coloring matter d, and returns an electron while it returns this electrolyte component (for example, I-), when charge transportation material is an electrolyte. By continuing irradiating light, a series of reactions occur succeedingly and can take out the electrical and electric equipment.

[0077] Hereafter, an usable material and its formation method are explained to each class of the

aforementioned optoelectric transducer. In addition, when calling it "a conductive base material" below, it is accepted conductive-layer 12, and although it consists of a conductive layer 12 and a substrate 26 which it is arbitrary and is prepared, when calling it a "counter electrode" including both sides, it is accepted counter electrode conductive-layer 20, and both sides are included although it consists of a counter electrode conductive layer 20 and a substrate 26 which it is arbitrary and is prepared.

[0078] (A) A conductive base material conductivity base material consists of the monolayer of (1) conductive layer or (2) conductive layers, and two-layer [of a substrate]. In the case of (1), material at which intensity and sealing performance are fully maintained as a conductive layer is used. For example, a metallic material (alloys containing these, such as platinum, gold, silver, copper, zinc, titanium, and aluminum) can be used. In the case of (2), the substrate which has the conductive layer which contains an electric conduction agent in a photosensitive-layer side can be used. As a desirable electric conduction agent, a metal (for example, alloys containing these, such as platinum, gold, silver, copper, zinc, titanium, aluminum, and an indium), carbon, or conductive metallic oxides (what doped a fluorine or antimony to an indium-tin multiple oxide and the tin oxide) are mentioned. The thickness of a conductive layer has desirable about 0.02-10 micrometers.

[0079] A conductive base material has surface electrical resistance as good as a low. Below 50ohms / ** of the range of surface electrical resistance are desirable, and it is more desirable. [of below 20ohms / **]

[0080] When irradiating light from a conductive base material side, as for a conductive base material, it is desirable that it is substantially transparent. It means substantially that permeability is it 10% or more that it is transparent in some or the whole region of light of a visible - near infrared region (400-1200nm), it is desirable that it is 50% or more, and 80% or more is more desirable. It is desirable that the permeability of the wavelength region where a photosensitive layer has sensitivity especially is high.

[0081] What formed the transparent conductive layer which consists of a conductive metallic oxide in the front face of transparent substrates, such as glass or plastics, by an application or vacuum evaporationo as a transparent conductivity base material is desirable. As a transparent conductive layer, the diacid-ized tin or indium-stannic-acid ghost (ITO) which doped a fluorine or antimony is desirable. A transparent polymer film besides glass substrates, such as an advantageous soda glass and an alkali free glass without the influence of alkali elution, can be used for a transparent substrate in respect of a low cost and intensity. As a material of a transparent polymer film, there is a triacetyl-cellulose (TAC), polyethylene-terephthalate (PET), polyethylenenaphthalate (PEN), syndiotactic polystyrene (SPS), polyphenylene-sulfide (PPS), polycarbonate (PC), polyarylate (PAr), polysulfone (PSF), polyester sulfone (PES), polyimide (PI), polyether imide (PEI), annular polyolefine, and bromine-ized phenoxy etc. In order to secure sufficient transparency, as for the coverage of a conductive metallic oxide, it is desirable to consider as per [0.01-100g] two 1m of base materials of glass or plastics.

[0082] It is desirable to use a metal lead in order to lower resistance of a transparent conductivity base material. The quality of the material of a metal lead has desirable metals, such as platinum, gold, nickel, titanium, aluminum, copper, and silver. As for a metal lead, it is desirable to prepare the transparent conductive layer which installs in a transparent substrate by vacuum evaporationo, sputtering, etc., and becomes it from the conductive tin oxide or a conductive ITO film on it. The fall of the amount of incident lights by metal lead installation may be 1 - 5% more preferably less than 10%.

[0083] (B) The photosensitive-layer aforementioned photosensitive layer absorbs light, performs charge separation, and has the function which produces an electron and an electron hole. The aforementioned photosensitive layer contains the semiconductor by which coloring matter sensitization was carried out. With the semiconductor by which coloring matter sensitization was carried out, generating of an optical absorption, the electron by this, and an electron hole takes place mainly in coloring matter, and a semiconductor bears the role which receives and transmits this electron (or electron hole). As for the semiconductor used by this invention, it is desirable that it is the n-type semiconductor which gives an anode current by a conductor electron serving as a carrier

under optical pumping.

[0084] (B-1) The compounds (for example, a strontium titanate, titanic-acid calcium, titanic-acid sodium, a barium titanate, a niobic-acid potassium, etc.) which have silicon, an element semiconductor like germanium, a III-V system compound semiconductor, metaled chalcogenide (for example, an oxide, a sulfide, selenides, or those composites etc.), or a perovskite structure as a semiconductor semiconductor can be used.

[0085] As chalcogenide of a desirable metal, the oxide of titanium, tin, zinc, iron, a tungsten, a zirconium, a hafnium, strontium, an indium, a cerium, an yttrium, a lanthanum, vanadium, niobium, or a tantalum, cadmium, zinc, lead, silver, antimony or the sulfide of a bismuth, cadmium or a leaden selenide, the telluride of cadmium, etc. are mentioned. As other compound semiconductors, the selenide of phosphides, such as zinc, a gallium, an indium, and cadmium, a gallium arsenide, or a copper-indium, the sulfide of a copper-indium, etc. are mentioned. Furthermore, the composite expressed with MxOySz or M1xM2yOz (the number [metallic element] of combination with which an oxygen atom, x, and y and z become as for M, M1, and M2, and, as for O, a valence becomes neutral, respectively) can also be used preferably.

[0086] As an example of the semiconductor used for this invention, Si, TiO2, SnO2, Fe 2O3, WO3, ZnO, Nb 2O5, CdS, ZnS and PbS, Bi2S3, CdSe, CdTe, SrTiO3, GaP, InP, GaAs, CuInS2, and CuInSe2 grade are desirable. TiO2, ZnO, SnO2, Fe 2O3, WO3 and Nb 2O5, CdS and PbS, CdSe, SrTiO3 and InP, GaAs, CuInS2, or CuInSe2 is more desirable, TiO2 or especially Nb 2O5 is desirable, and TiO2 is the most desirable. TiO2 has desirable TiO2 which includes an anatase type crystal 70% or more, and especially TiO2 of 100% anatase type crystal is desirable. Moreover, it is also effective to dope a metal in order to raise the electronic conductivity in these semiconductors. As a metal to dope, divalent and a trivalent metal are desirable. It is the purpose which prevents that a reverse current flows from a semiconductor to a charge transporting bed, and it is also effective to dope a univalent metal to a semiconductor.

[0087] Although a single crystal or a polycrystal is sufficient as the semiconductor used for this invention, viewpoints, such as a manufacturing cost, raw-material reservation, and an energy pay back time, to its polycrystal is desirable, and especially its porous membrane that consists of a semiconductor particle is desirable. Moreover, the amorphous portion may be included in part.

[0088] Generally the particle size of a semiconductor particle is the order of nm-mu m. As for the mean particle diameter of the primary particle which asked for projected area from the diameter when converting into a circle, it is desirable that it is 5-200nm, and its 8-100nm is more desirable. Moreover, the mean particle diameter of the semiconductor particle in dispersion liquid (aggregated particle) has desirable 0.01-30 micrometers. It is 10nm or less preferably [may mix two or more kinds of particles from which a particle size distribution differs, and / that the average size of a small particle is 25nm or less in this case], and more preferably. Particle size is big, for example, it is also desirable to mix a semiconductor particle (100nm or more and about 300nm) in order to scatter an incident light and to raise the rate of optical capture.

[0089] The number of the kinds of semiconductor particle one, and they may be two or more sorts of different mixtures. When mixing and using two or more sorts of semiconductor particles, as for one sort, it is desirable that they are TiO2, ZnO, Nb 2O5, or SrTiO3. Moreover, as one more sort, it is desirable that they are SnO2, Fe2O3, and WO3. As a still more desirable combination, combination, such as ZnO, SnO2, ZnO and WO3, or ZnO, SnO2, WO3, can be mentioned. When mixing and using two or more sorts of semiconductor particles, each particle size may differ. The particle size of the semiconductor particle especially mentioned at the one above-mentioned item is large, and combination with the small semiconductor particle mentioned henceforth [2 items] is desirable. The particle of a desirable large particle size is 100nm or more, and the particle of a small particle size is 15nm or less in combination.

[0090] As a method of producing a semiconductor particle, they are the company (1998) of the "science of sol-gel method" AGUNE ** style of ********, and a technical-information association.

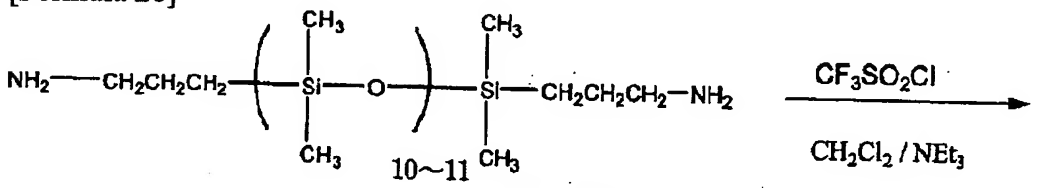
[Translation done.]

* NOTICES *

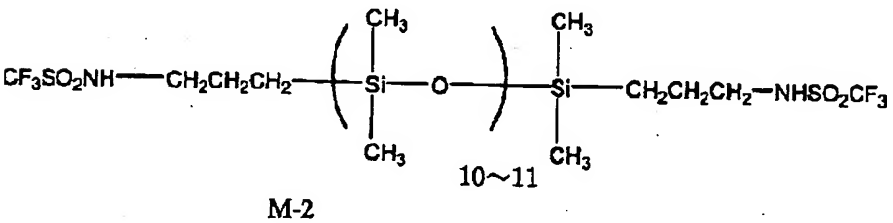
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

EXAMPLE

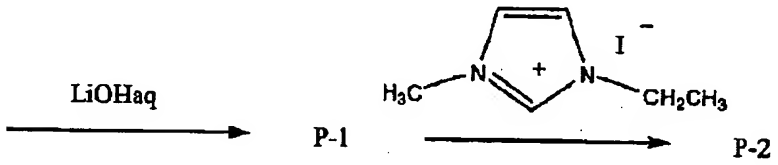
[Example] Hereafter, although an example explains this invention concretely, this invention is not limited at all by these examples.
[0177] (Example 1) Synthetic (1) instantiation compound P-1 of a compound, and composition of P-2
[0178]
[Formula 26]



M-1 平均分子量900－1000



M-2



[0179] ** After dissolving synthetic diamine (M-1) 18g of intermediate field M-2 in 50ml of methylene chlorides and adding truffe RUORO sulfonyl chloride 8.4g, it was dropped at -30 degrees C, having triethylamine 7 bet it for about 10 minutes. Under the room temperature, after stirring for 3 hours, 30ml of water was added to reaction mixture, liquid separation and 1-N hydrochloric-acid water washed the methylene-chloride phase, and reduced pressure distilling off of the methylene chloride was carried out after dryness with magnesium sulfate. The concentrate was refined in silica gel column chromatography (methylene chloride), and M-2 [10g] was obtained as oily matter.
[0180] ** Disulfon amide (M-2) 10g obtained by the synthetic above of P-1 was dissolved in THF50ml, 2O0.7g of LiOH-H and 5ml of water were added, and heating reflux was carried out for 30 minutes. Magnesium sulfate was added and filtered to reaction mixture, the methylene chloride was added for the filtrate after reduced pressure distilling off, reduced pressure distilling off of the filtrate which filtered insoluble matter was carried out again, and P-1 [6.0g] was obtained as colorless oily matter after dryness with the vacuum dryer. The structure check was performed by H1NMR and the methyl group on Si and the proton ratio of CH2CH2CH2 showed that it was the average 10 of n (average molecular weight 1192).
[0181] ** 5.0g (P-1) of synthetic screw lithium imide salts of P-2 was distributed in 20ml of methylene chlorides, and 20ml of water, iodation 1-ethyl-4-methyl imidazolium 2.0g was added, and it stirred for room temperature-ized 30 minutes. The methylene-chloride phase was separated and it

condensed after rinsing. The concentrate was refined in silica gel column chromatography, and P-2 [5.5g] was obtained as colorless oily matter.

[0182] (Example 2) The manufacture inside of photoelectrochemical-cell 2-1. titanium-dioxide dispersion liquid to the vessel made from stainless steel of 200ml of content volume which carried out Teflon (registered trademark) coating 15g (Degussamade from Japanese Aerosil P-25) of titanium dioxides, 45g of water, With 1g [of dispersants] (Aldrich make, Triton X-100) and a diameter of 0.5mm zirconia-beads (Nikkato Corp. make) 30g was put in, and it distributed in 1500rpm for 2 hours using the Sand-grinder mill (product made from eye MEKKUSU). Zirconia beads were filtered and removed from the distributed object. The mean particle diameter of the titanium dioxide in this case was 2.5 micrometers. The particle size at this time is measured in the master sizer made from MALVERN.

[0183] 2-2. The glass rod was used and the above-mentioned dispersion liquid were applied to the electric conduction side side of the electrically conductive glass (what carried out cutting processing of the TCO glass [by Asahi Glass Co., Ltd.]-U at the 20mmx20mm size) which coated the tin oxide which doped the creation fluorine of TiO2 electrode (electrode A) which adsorbed coloring matter. Under the present circumstances, the adhesive tape was stretched to the part by the side of an electric conduction side (from an edge to 3mm), and it considered as the spacer, and glass was put in order and it applied eight sheets at a time at once so that an adhesive tape might come to ends. After the application, it exfoliated and the adhesive tape was air-dried for one day at the room temperature. Next, this glass was put into the electric furnace (muffle furnace FP-32 type made from Yamato Science), and it calcinated for 30 minutes at 450 degrees C. It flooded with the ethanol solution (3xten - four mols/(l.)) of coloring matter R-1 for 3 hours, after taking out this glass and cooling. After being immersed in a 4-tert-butyl pyridine for 15 minutes, the air drying of the glass which coloring matter dyed was washed and carried out by ethanol. Thus, the thickness of the photosensitive layer obtained is 10 micrometers, and the coverage of a semiconductor particle was taken as 20 g/m2. In addition, the surface electrical resistance of electrically conductive glass was about 30ohm/**.

[0184] 2-3. The acetonitrile was distilled off, applying the acetonitrile solution (an acetonitrile being a constituent and a homogeneous amount) of the electrolyte constituent (E-102 to E-110) containing the compound or comparison compound of this invention shown in Table 1 to the TiO2 electrode substrate (1cmx1cm) which is the creation **** of a photoelectrochemical cell, and was made and created and by which the color sensitizing was carried out, and infiltrating it into TiO2 electrode under 60 degrees C and reduced pressure. The platinum vacuum evaporationo glass of the same size was laid on top of these electrodes, and the photoelectrochemical cell (sample B-102 to B-110) was obtained (Table 1, drawing 2). Moreover, after laying the electrolytic solution (E-101 of Table 1) using the solvent on top of the same TiO2 electrode substrate (2cmx2cm) as the above by which coloring matter sensitization was carried out with the platinum vacuum evaporationo glass of the same size as the electrode, it infiltrated the electrolytic solution into the crevice between both glass using capillarity, and created the photoelectrochemical cell (sample B-101). In addition, the cell (B-110) using the electrolyte E-110 containing the salt P-31 which has a polymerization nature machine performed heating at 80 degrees C after cell creation for 1 hour in order to carry out the polymerization of the electrolyte.

[0185] The photoelectrochemical cell by which the laminating of electrically conductive glass 1 (that by which the electric conduction agent layer 2 was ****(ed) on glass), TiO2 electrode 3, a pigment layer 4, an electrolyte 5, the platinum layer 6, and the glass 7 was carried out to order was created by this example as shown in drawing 2 .

[0186]

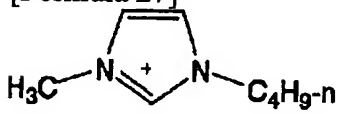
[Table 1]

電解質	組成（質量%）	サンプル	備考
E-101	RE-1 (48) /BCE (50) /I2 (2)	B-101	比較例
E-102	RE-1 (98) /I_2 (2)	B-102	比較例
E-103	RE-1 (48) /RE-2 (50) / I_2 (2)	B-103	比較例
E-104	RE-1 (48) /P-2 (50) / I_2 (2)	B-104	本発明
E-105	RE-1 (48) /P-3 (50) / I_2 (2)	B-105	本発明
E-106	RE-1 (48) /P-8 (50) / I_2 (2)	B-106	本発明
E-107	RE-1 (48) /P-10 (50) / I_2 (2)	B-107	本発明
E-108	RE-1 (48) /P-14 (50) / I_2 (2)	B-108	本発明
E-109	RE-1 (48) /P-21 (50) / I_2 (2)	B-109	本発明
E-110	RE-1 (48) /P-31 (48) / I_2 (2) /AIBN	B-110	本発明

BCE（溶媒）：ビスシアノエチルエーテル

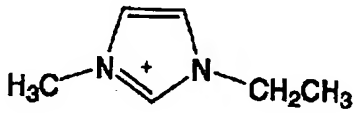
AIBN（熱重合開始剤）：アゾイソブチロニトリル

[0187]
[Formula 27]



I^-

RE-1



$^-N(SO_3CF_3)_2$

RE-2

[0188] 2-4. It is AM1.5 about the light of the xenon lamp of measurement 500W of a photoelectric conversion efficiency (USHIO make). By letting a filter (product made from Oriel), and a sharp cut filter (KenkoL-41) pass, the simulation sunlight which does not include ultraviolet rays was generated and this luminous intensity was adjusted to 100 mW/cm2.
[0189] The crocodile clip was connected to the above-mentioned electrically conductive glass and above-mentioned platinum vacuum evaporationo glass of a photoelectrochemical cell, respectively, and the electrical and electric equipment which irradiated simulation sunlight and was generated at 45 degrees C was measured in the current-potential measuring device (case rhe SMU238 type). the open circuit voltage (Voc) of the photoelectrochemical cell called for by this, short-circuit current density (Jsc), and a form factor -- (FF) [= maximum output/(open-circuit-voltage x short-circuit current)] and a conversion efficiency (eta), and constant temperature -- the decreasing rate of the short-circuit current density after carrying out the passage of time for 400 hours was collectively indicated to Table 2 under constant humidity (60 degrees C, 70%R.H.)
[0190]
[Table 2]

サンプル	Jcs (mA/m²)	Voc (V)	FF	η (%)	Jsc低下率 (%) 60℃－湿度70% 400時間	備考
B-101	10.1	0.66	0.64	4.3	99	比較例
B-102	7.8	0.6	0.65	3.0	11	比較例
B-103	9.2	0.64	0.68	4.0	21	比較例
B-104	11.1	0.65	0.67	4.8	5	本発明
B-105	10.6	0.64	0.68	4.6	7	本発明
B-106	10.5	0.67	0.65	4.6	8	本発明
B-107	12.1	0.64	0.64	5.0	8	本発明
B-108	10.6	0.65	0.64	4.4	6	本発明
B-109	9.9	0.64	0.68	4.3	7	本発明
B-110	9.5	0.68	0.62	4.0	4	本発明

Jsc：短絡電流密度、Voc：開放電圧、FF：形状因子、η：変換効率

[0191] Since a solvent volatilizes, the photoelectrochemical cell (B-101) using the comparison electrolytic solution using the solvent has very bad endurance. Moreover, the comparison sample (B-

102, B-103) using fused salt RE-1 and/or RE-2 passes, and although degradation in the time is small, a photo-electric-translation performance is not enough [degradation]. When the salt of this invention is used to them, initial performances, such as short-circuit current density and a conversion efficiency, and endurance are excellent. Such an effect was seen when which coloring matter was used.

[0192] (Example 3) As a creation positive active material of a lithium rechargeable battery 3-1. positive-electrode sheet LiCoO2 43 mass sections, the scale-like graphite 2 mass section, the acetylene black 2 mass section, Furthermore, add the polyacrylonitrile 3 mass section as a binder, and the slurry which kneaded the acrylonitrile 100 mass section as a medium, and was obtained is painted on an aluminum foil with a thickness of 20 micrometers using an extrusion formula application machine. After pressing with the calender press machine after dryness, the lead board made from aluminum was welded to the edge, and the positive-electrode sheet with 95 micrometers [in thickness] and a width-of-face [of 54mm] x length of 49mm was created.

[0193] 3-2. as the creation negative-electrode active material of a negative-electrode sheet -- a meso face pitch system carbon material (PETOKA) -- as 43 mass sections and an electric conduction agent -- the acetylene black 2 mass section and the graphite 2 mass section -- comparatively -- coming out -- mixing -- further -- as a binder -- a polyacrylonitrile -- 3 mass sections -- adding -- the N-methyl pyrrolidone 100 mass section -- as a medium -- kneading -- a negative electrode -- a mixture -- the slurry was obtained a negative electrode -- a mixture -- the slurry was painted on copper foil with a thickness of 10 micrometers using the extrusion formula application machine, it pressed with the calender press machine after dryness, and the negative-electrode sheet with 46 micrometers [in thickness] and a width-of-face [of 55mm] x length of 50mm was created After welding the lead board made from nickel to the edge of a negative-electrode sheet, it heat-treated at 230 degrees C for 1 hour in dry air of -40 degrees C or less of dew-points. Heat treatment was performed using the far-infrared heater.

[0194] The creation negative-electrode sheet of a 3-3. sheet cell and the positive-electrode sheet carried out dehydration dryness at 230 degrees C for 30 minutes in dry air of -40 degrees C or less of dew-points, respectively. In dry atmosphere, the laminating of the separator (polyethylene porosity film) and nonwoven fabric which were judged in a dried [dehydration] positive-electrode sheet with a width-of-face [of 54mm] x length of 49mm and width-of-face [of 60mm] x length of 60mm was carried out, the liquid which dissolved the electrolyte (E-202-213) of the composition shown in Table 3 in the acetonitrile of the amount of said was applied on the nonwoven fabric, and the acetonitrile was distilled off under reduced pressure at 50 degrees C Moreover, the electrolytic solution (E-201) using the solvent was infiltrated into the nonwoven fabric as it is. The laminating of the dried [dehydration] negative-electrode sheet with a width-of-face [of 55mm] x length of 50mm was carried out on it, using the sheathing material which consists of a laminate film of a polyethylene (50 micrometers)-polyethylene terephthalate (50 micrometers), heat weld was carried out, four edges were sealed under the vacuum, and the sheet type cell (B-201 to B-213) was created. In addition, the cell (B-209) using the electrolyte E-209 containing the salt P-30 which has a polymerization nature machine performed heating at 80 degrees C after cell creation for 1 hour in order to carry out the polymerization of the electrolyte. The composition of the sheet cell created by this example is shown in drawing 3 .

[0195]

[Table 3]

電解質番号	電解質組成（質量%）	電池番号	備考
E-201	RE-3 (30) /PC (30) /EC (40)	B-201	比較例
E-202	RE-3 (30) /RE-2 (70)	B-202	比較例
E-203	$LiBF_4$ (30) /RE-2 (70)	B-203	比較例
E-204	P-1 (100)	B-204	本発明
E-205	P-5 (100)	B-205	本発明
E-206	P-9 (100)	B-206	本発明
E-207	P-13 (100)	B-207	本発明
E-208	P-18 (100)	B-208	本発明
E-209	P-30 (98) /AIBN (2)	B-209	本発明
E-210	P-1 (30) /RE-3	B-210	本発明
E-211	P-5 (30) /RE-3	B-211	本発明

E-212	P-1 (30) /PEO	B-212	本発明
E-213	P-5 (30) /PEO	B-213	本発明

PC：プロピレンカーボネート

EC：エチレンカーボネート

RE-3 : $LiN(SO_2CF_3)_2$

PEO : $-(CH_2CH_2O)_n-$ (平均分子量 3000)

[0196] 3-4. About the sheet type cell created by the evaluation aforementioned method of a cell performance, charge and discharge were repeated 30 times on condition that current density 1.3 mA/cm2, charge final-voltage 4.2V, and discharge-final-voltage 2.6V**, and the service capacity in 30 cycle eye was calculated. This was investigated about five cells of the same prescription, and the average was made into the capacity of the cell. Thus, the capacity of each cell was calculated and the relative capacitor to SB-1 was calculated. Moreover, the service capacity of a 200 cycle eye was calculated about each cell, the ratio to the service capacity of 10 cycle eye was calculated, and it expressed as a cycle capacity. Each value was shown in Table 4.

[0197]

[Table 4]

電池番号	相対容量	サイクル容量	備考
B-201	1	0.28	比較例
B-202	0.61	0.87	比較例
B-203	0.33	0.78	比較例
B-204	0.84	0.98	本発明
B-205	0.72	0.95	本発明
B-206	0.81	0.96	本発明
B-207	0.85	0.98	本発明
B-208	0.94	0.95	本発明
B-209	0.66	0.95	本発明
B-210	0.95	0.94	本発明
B-211	0.91	0.94	本発明
B-212	0.93	0.93	本発明
B-213	0.90	0.95	本発明

[0198] The above-mentioned result shows that the electrolyte constituent of this invention is raising cycle nature, without seeing the big fall of capacity.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the outline block diagram showing an example of the optoelectric transducer of this invention.

[Drawing 2] It is the cross section showing the composition of the photoelectrochemical cell created in the example 2.

[Drawing 3] It is drawing showing the composition of the sheet type cell created in the example 3.

[Description of Notations]

1 Electrically Conductive Glass
2 Electric Conduction Agent Layer
3 TiO2 Electrode
4 Pigment Layer
5 Electrolyte
6 Platinum Layer
7 Glass
10 Optoelectric Transducer
12 Conductive Layer
14 Under Coat
16 Photosensitive Layer
18 Charge Transporting Bed
20 Counter Electrode Conductive Layer
24 Semiconductor Layer
28 Substrate
31 Positive-Electrode Sheet
32 Solid Polymer Electrolyte
33 Negative-Electrode Sheet
34 Positive-Electrode Terminal
35 Negative-Electrode Terminal
s Semiconductor particle
d Coloring matter
t Charge transportation material

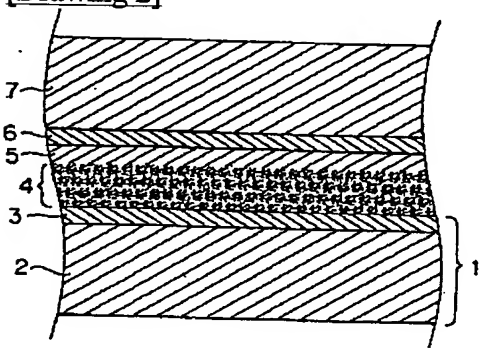
[Translation done.]

* NOTICES *

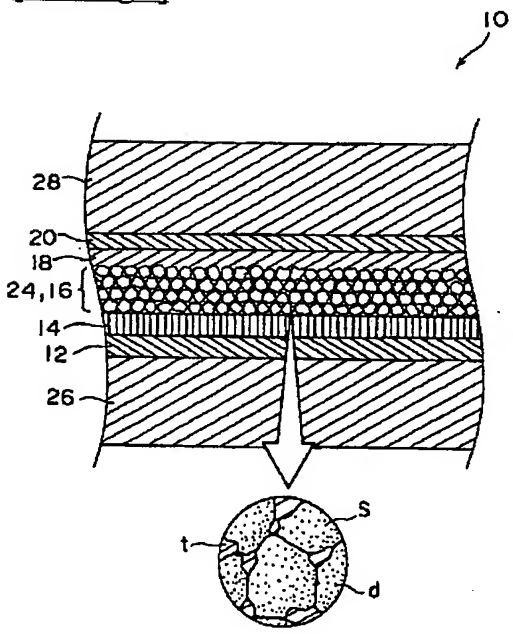
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

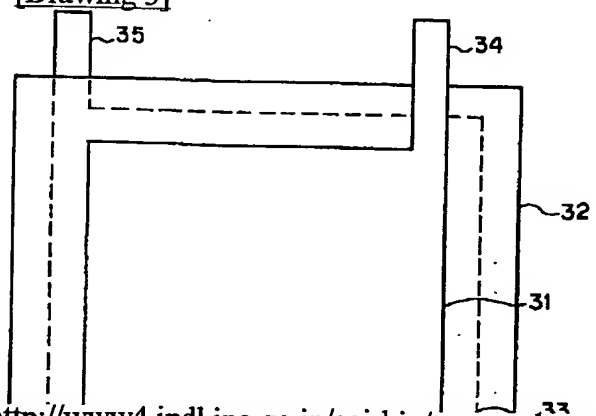
[Drawing 2]

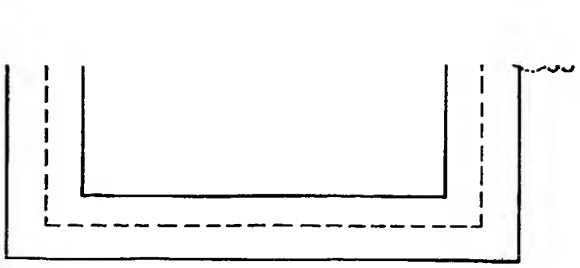


[Drawing 1]



[Drawing 3]





[Translation done.]